PB80-177728

Worker Reentry in Florida Citrus
Pesticides in the Agricultural Environment

Agricultural Research and Education Center
Lake Alfred, FL

Prepared for

Health Effects Research Lab.
Research Triangle Park, NC

Feb 80

U.S. Department of Commerce
National Technical Information Service
NTIS.

United States
Environmental Protection
Agency

Health Effects Research
Laboratory
Research Triangle Park NC 27711

EPA-600/1-80-013
February 1980

Research and Development

PB80-177728

EPA

Worker Reentry in Florida Citrus Pesticides in the Agricultural Environment

REPRODUCED BY
NATIONAL TECHNICAL
INFORMATION SERVICE
U. S. DEPARTMENT OF COMMERCE
SPRINGFIELD, VA. 22161

RESEARCH REPORTING SERIES

Research reports of the Office of Research and Development, U.S. Environmental Protection Agency, have been grouped into nine series. These nine broad categories were established to facilitate further development and application of environmental technology. Elimination of traditional grouping was consciously planned to foster technology transfer and a maximum interface in related fields. The nine series are:

1. Environmental Health Effects Research
2. Environmental Protection Technology
3. Ecological Research
4. Environmental Monitoring
5. Socioeconomic Environmental Studies
6. Scientific and Technical Assessment Reports (STAR)
7. Interagency Energy-Environment Research and Development
8. "Special" Reports
9. Miscellaneous Reports

This report has been assigned to the ENVIRONMENTAL HEALTH EFFECTS RESEARCH series. This series describes projects and studies relating to the tolerances of man for unhealthful substances or conditions. This work is generally assessed from a medical viewpoint, including physiological or psychological studies. In addition to toxicology and other medical specialities, study areas include biomedical instrumentation and health research techniques utilizing animals — but always with intended application to human health measures.

This document is available to the public through the National Technical Information Service, Springfield, Virginia 22161.

TECHNICAL REPORT DATA
(Please read Instructions on the reverse before completing)

1. REPORT NO. EPA-600/1-80-013	2.
3. RECIPIENT'S ACCESSION NO. PB 80 177728	
4. TITLE AND SUBTITLE: Worker Reentry in Florida Citrus Pesticides in the Agricultural Environment	5. REPORT DATE: February 1980
	6. PERPORMING ORGANIZATION CODE
7. AUTHOR(S): H.N. Nigg	8. PERFORMING ORGANIZATION REPORT NO.
9. PERFORMING ORGANIZATION NAME AND ADDRESS: University of Florida, Institute of Food and Agricultural Sciences, P.O. Box 1088, Lake Alfred, FL 33850	10. PROGRAM ELEMENT NO. 1EA615
	11. CONTRACT/GRANT NO. R-804633
12. SPONSORING AGENCY NAME AND ADDRESS: Health Effects Research Laboratory, U.S. Environmental Protection Agency, Research Triangle Park, NC 27711	13. TYPE OF REPORT AND PERIOD COVERED
	14. SPONSORING AGENCY CODE EPA 600/11
15. SUPPLEMENTARY NOTES	

16. ABSTRACT

The environmental behavior of five organophospate insecticides in Florida citrus are reported. Parathion disappearance rate from fruit, leaf, and soil surfaces was the same. Potential worker exposure to parathion was leaf surface > soil surface >> fruit surface and a minor component in air. Disappearance of parathion surface residues was accurately represented with a first-order solar radiation, rainfall, temperature, and dew model.

Dialifor, malathion, oxydemetonmethyl, and dioxathion fruit and leaf surface residues exhibited different disappearance rates. The disappearance rate, however, was the same on fruit and leaf surfaces for individual compounds. Based on rates of disappearance under different environmental conditions, environmental sensitivity was oxydemetonmethyl malathion dioxathion dialifor. These data suggest that fruit data could be eliminated from worker safety reentry registration requirements for organophosphate insecticides.

Two surface residue techniques were compared. Vacuum and dislodgeable residue techniques differed in the amount of particulate matter and pesticide residue recovered. Vacuum, dislodgeable and air particulate numbers and sizes were relatively comparable. The dislodgeable residue technique for worker reentry data appeared superior to the vacuum technique.

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group
Organophosphate insecticide Citrus workers Leaf/soil/fruit surfaces	Parathion Dialifor Malathion Oxydemetonmethyl Dioxathion Toxicology	06F,T

18. DISTRIBUTION STATEMENT: RELEASE TO PUBLIC	19. SECURITY CLASS *(This Report)* UNCLASSIFIED	21. NO. OF PAGES
	20. SECURITY CLASS *(This page)* UNCLASSIFIED	22. PRICE

EPA Form 2220-1 (Rev. 4-77) PREVIOUS EDITION IS OBSOLETE

EPA-600/1-80-013
February 1980

WORKER REENTRY IN FLORIDA CITRUS
PESTICIDES IN THE AGRICULTURAL ENVIRONMENT

by

H. N. Nigg
University of Florida
Institute of Food and Agricultural Sciences
Agricultural Research and Education Center
Post Office Box 1088
Lake Alfred, FL 33850

Grant Number R-804633

Project Officer

J. E. Davis
Environmental Toxicology Division
Health Effects Research Laboratory
Research Triangle Park, NC 27711

U.S. ENVIRONMENTAL PROTECTION AGENCY
OFFICE OF RESEARCH AND DEVELOPMENT
HEALTH EFFECTS RESEARCH LABORATORY
RESEARCH TRIANGLE PARK, NC 27711

DISCLAIMER

This report has been reviewed by the Field Studies Section, U.S. Environmental Protection Agency, and approved for publication. Approval does not signify that the contents necessarily reflect the views and policies of the U.S. Environmental Protection Agency, nor does mention of trade names or commercial products constitute endorsement or recommendation for use.

FOREWARD

The many benefits of our modern, developing, industrial society are accompanied by certain hazards. Careful assessment of the relative risk of existing and new man-made environmental hazards is necessary for the establishment of sound regulatory policy. These regulations serve to enhance the quality of our environment in order to promote the public health and welfare and the productive capacity of our nation's population.

The Health Effects Research Laboratory, Research Triangle Park, conducts a coordinated environmental health research program in toxicology, epidemiology, and clinical studies using human volunteer subjects. These studies address problems in air pollution, non-ionizing radiation, environmental carcinogenesis and the toxicology of pesticides as well as other chemical pollutants. The Laboratory participates in the development and revision of air quality criteria documents on pollutants for which national ambient air quality standards exist or are proposed, provides the data for registration of new pesticides or proposed suspension of those already in use, conducts research on hazardous and toxic materials, and is primarily responsible for providing the health basis for non-ionizing radiation standards. Direct support to the regulatory function of the Agency is provided in the form of expert testimony and preparation of affidavits as well as expert advice to the Administrator to assure the adequacy of health care and surveillance of persons having suffered imminent and substantial endangerment of their health.

The persistence of pesticide residues and their toxic conversion products on foliage, soil, and fruit must be considered when one estimates the period required for safe reentry of workers into orchards after spraying. Fruit residues are also necessary to establish the necessary period between spraying and harvest so that harmful levels of these materials are eliminated. This report describes research that resulted in a weather model which allows one to predict the rate of decay of a number of organophosphorus pesticides and their toxic conversion products over a wide range of weather conditions. Use of this model will allow the determination of safer reentry and preharvest intervals for these and similar pesticides than was possible using a simple model of decay with time.

F. G. Hueter, Ph.D.
Acting Director
Health Effects Research Laboratory

ABSTRACT

The environmental behavior of five organophosphate insecticides in Florida citrus are reported. The parathion disappearance rate from fruit, leaf, and soil surfaces was the same. The potential worker exposure to parathion was leaf surface > soil surface >> fruit surface and a minor component in air. The disappearance of parathion surface residues was accurately represented with a first-order solar radiation, rainfall, temperature, and dew model. Malathion residue in the rind of five varieties of citrus fruit had a half-life of 8 days and malathion disappearance was accurately described with weather.

Dialifor, malathion, oxydemetonmethyl and dioxathion fruit and leaf surface residues exhibited different disappearance rates. The disappearance rate, however, was the same on fruit and leaf surfaces for individual compounds. Based on rates of disappearance under different environmental conditions, environmental sensitivity was oxydemetonmethyl > malathion > dioxathion > dialifor. These data suggest that fruit data could be eliminated from worker safety reentry registration requirements for organophosphate insecticides.

Two surface residue techniques were compared. The vacuum and dislodgeable residue techniques differed in the amount of particulate matter and pesticide residue recovered. Vacuum, dislodgeable and air particulate numbers and sizes were relatively comparable. Few particles above 45 μ were found on leaf surfaces and in air and relative numbers and sizes were related to soil particulates. Airborne transfer of soil particulates to leaf surface to worker was suggested. The dislodgeable residue technique for worker reentry data appeared superior to the vacuum technique.

CONTENTS

Foreword.....iii
Abstract..... iv
List of Figures..... vi
List of Tables.....vii
Abbreviations and Symbols.....viii
Acknowledgements..... ix

I. Introduction..... 1
II. Conclusions..... 2
III. Recommendations..... 3
IV. Experimental Procedures..... 4
Large plot parathion experiment..... 4
Malathion fruit experiment..... 7
Residue technique experiment..... 8
Small plot experiment..... 8
V. Results and Discussion..... 10
Large plot parathion experiment..... 10
Fruit and leaf residues..... 10
Cover crop residues..... 14
Soil surface residues..... 15
Residues in ambient air..... 15
Total residues..... 15
Malathion fruit experiment..... 19
Residue technique experiment..... 21
Small plot experiment..... 36

References..... 49
Bibliography..... 53

LIST OF FIGURES

Number		Page
1	Weather Model of Emulsifiable Concentrate (EC) and Wettable Powder (WP) Parathion Disappearance on 'Valencia' Orange Leaves and Fruit	11
2	Weather Model of Emulsifiable Concentrate (EC) and Wettable Powder (WP) Parathion Disappearance on the Soil Surface of Astatula Fine Sand Between Trees	17
3	Parathion in Ambient Air	17
4	Percentage of Parathion and Paraoxon Residues in Air on 'Valencia' Orange Leaves, on 'Valencia' Orange Fruit, and on the Soil Surface	18
5	Malathion in Fruit Rind	19
6	Small Plot-Cum. Weather Variables vs. Time in Days	37
7	Ln-Ln Plot of Combined Malathion Fruit and Leaf Surface Residues	43
8	Ln-Ln Plot of Combined Dialifor Fruit and Leaf Surface Residues	43
9	Ln-Ln Plot of Combined Dioxathion Fruit and Leaf Surface Residues	44
10	Ln-Ln Plot of Combined Oxydemetonmethyl Fruit and Leaf Surface Residues	44
11	% Malaoxon Residue	45

LIST OF TABLES

Number		Page
1	Simple Correlation Matrix for WP Parathion Residues and Environmental Variables	12
2	Simple Correlations for EC Parathion Residues and Environmental Variables	13
3	Simple Correlations for WP Paraoxon Residues and Environmental Variables	13
4	Simple Correlations for EC Paraoxon Residues and Environmental Variables	14
5	Multiple Linear Regression of Parathion and Paraoxon Residues and Environmental Variables	16
6	Malathion First-Order Residue Behavior in Florida Citrus Varieties Base on Time Alone and Time Plus Weather	20
7	Variables Used as Base for First-Order Model of Malathion Residue Disappearance	21
8	Comparison of 0.8 μ and 5.0 μ Filters with Parathion WP	22
9	Comparison of 5.0 μ and Glass Fiber Filters with Parathion WP	24
10	Filter Flow Characteristics	27
11	Comparison of WP and EC Formulations of Parathion	29
12	Vacuumed Particulates Size Analyses 0.8 μ Filter--Day 1 Post Application	31
13	Vacuumed Particulates Size Analyses 5.0 μ Filter--Day 1 Post Application	32
14	Filtered Aqueous Samples Particulate Size Analyses (0.22 μ)--Day 1 Post Application	34
15	Soil Particulate Distribution in Florida Citrus Soils	35
16	Small Plot Experiment 1.--Pesticide Residues	38
17	Small Plot Experiment 2.--Pesticide Residues	41
18	Small Plot--Fruit and Leaf Surface Residues--Coefficient of Variation	47
19	Conversion of Pesticide Application Rates from English to Metric System	48

LIST OF ABBREVIATIONS AND SYMBOLS

AI	--active ingredient
CAT	--cumulative average temperature
CLW	--cumulative leaf wetness
CR	--cumulative rainfall
CS	--cumulative solar radiation
EC	--emulsifiable concentrate
fpm	--feet per minute
g	--gram(s)
h or hr	--hour(s)
ha	--hectares
HDD	--heating degree days
kHz	--kilohertz
ℓ	--liter
lb or lbs	--pound(s)
LW	--leaf wetness (dew)
μ	--micron
$\mu g/cm^2$	--micrograms per square centimeter
$\mu g/m^3$	--micrograms per cubic meter
mℓ	--milliliter
ppm	--parts per million
S.D.	--standard deviation
WP	--wettable powder

ACKNOWLEDGEMENTS

The technical assistance of S. Cabrera, L. Economu, J. Keller, J. Lawrence, and D. Steele in the field and R. Surrency, M. Swift, J. Towne, M. Tynes, and R. Woodruff in the laboratory is gratefully acknowledged.

SECTION I

INTRODUCTION

Recurring harvester organophosphate intoxications in the Western United States have forced interest in the components of a worker reentry pesticide illness. These components have been identified as (1) application of an organophosphate insecticide; (2) conversion of the organophosphate to its 'oxon' metabolite; (3) dusty conditions in the field so as to provide for transfer of the pesticide to the worker; and (4) suitable weather conditions so that high levels of the pesticide persist on the leaf and soil surfaces.

The current approach to regulations to protect the worker has been to establish a worker reentry time. A worker reentry time is the time workers must wait after a pesticide application before reentering a treated field. These times range from 24 to 48 hours nationally and are as much as 60 days in California where stringent reentry regulations have been set by the California Department of Agriculture. The fact that California has recurring problems, however, does not mean that a problem exists in the rest of the U.S. Yet it is agreed that worker safety reentry regulations are necessary on a national basis to protect farm labor from adverse pesticide exposure.

Regardless of pesticide applied and a dusty environment, weather conditions are the key factor in oxon metabolite production and residue levels on leaf and soil surfaces after a pesticide application. This study focused on the poorly understood relationship between weather conditions and organophosphate residue levels.

SECTION II

CONCLUSIONS

1 The rate of disappearance of parathion and paraoxon from leaf, fruit, and soil surfaces was essentially the same.

2 The rates of disappearance of dialifor, malathion, oxydemetonmethyl, or dioxathion residues were identical from leaf and fruit surfaces for an individual compound. Different compounds had different dissipation rates.

3 The rate of disappearance of EC and WP formulations was the same. Differences in surface residue levels between EC and WP formulations appeared to be the result of initial deposits of pesticide.

4 Weather modeling of residue disappearance from surfaces was 50% more accurate as compared to the time model.

5 Weather modeling of malathion fruit residues indicated that prediction of food commodity residues may be a valid approach.

6 Recoveries of surface pesticide residues depended on the stringency of the method. For current regulatory purposes, the Gunther dislodgeable residue technique produces residues consistent with total possible exposure for both the parent and oxon metabolite.

7 The rate of disappearance was the same for leaf, soil, and leaf surfaces for parathion and for leaf and fruit surfaces for malathion, oxydemetonmethyl, dialifor, and dioxathion. Fruit surface residue data required for registration of pesticides could be eliminated.

8 Potential exposure of fruit pickers to parathion was greatest on the leaf surface, less on the fruit surface and very small in air.

SECTION III

RECOMMENDATIONS

1 The effect of individual weather variables on pesticide disappearance from surfaces should be studied. Such studies should include individual effects of temperature, solar radiation, and water and their confounded effects on pesticide disappearance from surfaces.

2 A better kinetic model for pesticide behavior should be sought. This model should have a firm theoretical foundation based on a physical or chemical process.

3 Investigations of the effect of chemical and physical characteristics such as hydrolysis, vapor pressure, photolysis, diffusion coefficient, and oxidation on residue behavior should be conducted.

4 Environmental factors responsible for the production of oxon metabolites of organophosphate insecticides should be further investigated.

5 Correlation of surface organophosphate residues, surface dust levels, and field worker exposure should be sought. This will allow accurate prediction of worker exposure.

6 A systematic modeling approach including all of the above factors should be taken to provide a rational basis for regulations.

SECTION IV

EXPERIMENTAL PROCEDURES

LARGE PLOT PARATHION EXPERIMENT

A mature 'Valencia' grove in excellent horticultural condition owned by the University of Florida was used for these experiments. This grove is not irrigated and is typical of the approximately 400,000 acres (162,000 ha) of 'Valencia' orange groves in Florida. Parathion emulsifiable concentrate (EC) and wettable powder (WP) were applied in separate treatments at a rate of 4 lbs active ingredient (AI)/acre in 750 gal of water* (4.48 kg AI/ha in 285 dkl) with an air-blast sprayer. Each treatment was replicated four times in a random block design including four no-spray control blocks. Two buffer rows were left unsprayed between each 48-tree replicate. Three individual experiments were carried out using the same plots. Experiment 1 was conducted from Jan. 1 to Mar. 1, 1977; experiment 2 from July 12 to Aug. 2, 1977; and experiment 3 from Oct. 1 to Dec. 14, 1977.

Orange fruit and leaf samples were collected as described by Gunther et al. (1973), Westlake et al. (1973), and Iwata et al. (1977) except that eight fruit per plot were collected. Random cover crop samples were obtained by carefully clipping leafy portions of the cover crop into glass leaf-punch bottles. Plots were sampled on days 1, 3, 5, 7, and then at weekly intervals until residue levels were below 0.005 $\mu g/cm^2$ for 2 consecutive sampling days.

Soil samples were collected by vacuum using the method of Spencer et al. (1975, 1977) except that a 40-mesh screen was used so that at least 10 g of soil could be obtained. Five 20 x 20 cm areas were vacuumed per sample. A dripline and a middle (between trees) sample was obtained from each plot. These samples were not random samples in that areas previously sampled were marked with stakes so that no resampling occurred.

Mini-personnel samplers (Andersen 2000, Inc., P. O. Box 7500, Salt Lake City, UT 84107) were used to obtain dislodged samples by attaching the sampler to a pole and sweeping the foliage for 5 min.

Ambient air was sampled for parathion by using Smith-Greenburg impingers as described by Sherma and Shafik (1975). Air flow was monitored at the beginning and end of each 4-hour sample with a Gilmont Model No. F1400 flowmeter (Roger Gilmont, Instr., Great Neck, NY 11021). Two-hundred mℓ

*Because of common usage, spray application rates will be given in the English system. Refer to Table 19 for conversion.

of ethylene glycol was used per impinger. A prefilter was not used so ambient air samples represent a combination of the vapor phase and airborne particulate parathion. Air samples were taken from 10 a.m. to 2 p.m. each sampling day. All other sampling was begun at 9:30 a.m. and ended at approximately 11:00 a.m. each sampling day.

Leaf and cover crop samples were processed as described by Gunther et al. (1974) as modified by Nigg et al. (1977a). The Sur-Ten solution was 2 mℓ of a 1:50 dilution of Sur-Ten per 1.0 ℓ of water. Fruit were clipped in the field into 2.5-gal (9.48 ℓ) pickle jars. Fruit were rolled twice in the same pickle jar at 70 rpm for 5 min in 200 mℓ of Sur-Ten solution to obtain dislodgeable fruit residues. Two 40 mℓ methylene chloride extractions were used to recover parathion and paraoxon from fruit washes.

Dust levels on leaf and fruit surfaces were determined by filtering leaf and fruit washes through preweighed Whatman #1 filter paper after extraction with methylene chloride. Filters were dried at room temperature, reweighed, and the dust level calculated in $\mu g/cm^2$ of surface (Westlake et al., 1973; Popendorf et al., 1975).

Soil samples were mixed by hand shaking and a 10-g subsample was weighed into a 100 mℓ beaker. Two mℓ of water was used to wet the 10 g of soil; the beaker was covered with aluminum foil and placed at 4°C. After 16 to 18 hr, 40 mℓ of acetone was added to the beaker and the soil was sonicated for 30 sec at 15,000 kHz. The beaker was immediately recovered with aluminum foil and the sediment allowed to settle for 5 min. A 20 mℓ aliquot was evaporated in a 50 mℓ volumetric flask under N_2 at 50°C almost to dryness. After cooling for approximately 5 min, 5 mℓ of benzene was added, followed by 40 mℓ of 2% sodium sulfate. The volumetric flask was capped, shaken vigorously, the layers allowed to separate, and the benzene layer brought into the neck of the flask with distilled water. The benzene layer was removed by pipette to a brown bottle over a few grams of Na_2SO_4. Benzene used for these extractions and all solvents used in subsequent extractions were gas chromatographic grade.

Mini-sampler impinger plates were extracted by rinsing each plate three times in 10 mℓ benzene, evaporating the benzene to 10 mℓ, and transferring the benzene to a brown bottle over Na_2SO_4. The glass fiber filters were inserted into brown bottles and 10 mℓ of benzene added to the bottle.

Ambient air samples were processed by the method of Sherma and Shafik (1975). Processed samples were stored for less than 14 days at-20°C prior to gas-liquid chromatographic (GLC) analysis.

Recoveries (mean $\pm$ S.D.) by these methods were: fortified Sur-Ten washes, parathion 99 $\pm$ 3%, paraoxon 94 $\pm$ 4%; fortified soil, parathion 97 $\pm$ 2%, paraoxon 92 $\pm$ 2%; fortified ethylene glycol, parathion 100 $\pm$ 3%, paraoxon 98 $\pm$ 2%.

Samples were analyzed by GLC with a flame photometric (FPD) phosphorous detector on a Tracor 550 GC. The 0.8 m X 2 mm inside diameter (I.D.) silylated glass column was packed with 5% SP2100 on 100/120 mesh Gaschrom Q (GCQ) (Supelco, Inc., Belefonte, PA 16823). Operating conditions were: injection port 210°C, column 190°C, detector 170°C, N_2 carrier gas flow 60 mℓ/min. Selected samples were also chromatographed on a 5% OV-210, 100/120 mesh GCQ column at 170°C for confirmation of identity and quantity of detected materials.

After GLC analysis, samples of each type were combined and subjected to high-performance liquid chromatography (HPLC), thin-layer chromatography (TLC), column chromatography, and GLC-mass-spectral analyses. Paraoxon was confirmed in each combined type sample by its GLC retention time on a 1.5 m X 2mm I.D. glass column packed with 3% SP2100 on 100/120 mesh Supelcoport at 200°, 30 mℓ/min helium flow and by comparison of the mass spectra of peaks eluting at approximately 5 min with that of a known sample of paraoxon. Details have been previously described (Nigg et al., 1977, 1978).

Both sides of the leaf punch were used for calculating residue concentration in $\mu g/cm^2$. For fruit areas, the diameter and length measurement of each fruit were used for an area calculation of an oblate, prolate, or regular sphere on a Wang 720C computer (Buslig, 1978). Other statistical methods, computer programs, the heating-degree day transformation, and the first-order weather-time model have been previously described (Nigg et al., 1977 a,b).

The percent total residue calculation used 240 X $10^6 cm^2$ of leaf surface area (Gunther et al., 1973; Turrell, 1961; Wilson, 1978) 20.4 x $10^6 cm^2$ of soil surface, and 9,850 m^3 of air per 48 tree plot. Total fruit surface per plot was calculated using actual fruit production times the average fruit surface area. These values were: 9.3 x $10^6 cm^2$ of fruit surface (exp. 1); 5.9 x $10^6 cm^2$ of fruit surface (exp. 2); and 8.6 x $10^6 cm^2$ of fruit surface (exp. 3). These values are based on a 48-tree plot containing 4.9-m tall trees spaced 7.6 m x 7.6 m. The percentage of the total residue in each ecosystem component was obtained by calculating the residue in each component and dividing by the total. It was assumed that the concentration of parathion in air was homogeneous. The average of WP and EC dripline and middle residue determinations was used as the soil residue value. Diffusion kinetics and mass transfer processes were ignored for this calculation.

Rainfall, temperature, and leaf wetness methods have been reported (Nigg et al., 1977a). For total solar incidence, a Matrix MK 1-G solarimeter (Matrix, Inc., Mesa, AZ 85201) was used. This solarimeter was calibrated by triangulation on a clear day assuming 0.8 transmissivity according to the equation:

$$I(\text{cal cm}^{-2}\text{min}^{-1}) = (2 \text{ cal cm}^{-2}\text{min}^{-1})\ 0.8^{\csc\Theta}\ \sin\Theta,$$

where Θ is the solar elevation angle (Schultze, 1976). Determinations were obtained from 11:30 a.m. to 12:45 p.m. EST at 15 min intervals for this calibration.

MALATHION FRUIT EXPERIMENT

A completely randomized design with four replications per treatment including four unsprayed check blocks was utilized in this study. Each experimental plot consisted of one city block. Within each plot, 3 to 10 trees of each citrus variety were used as source trees for an 8-fruit sample of grapefruit, lemon, tangerine, Temple, and 'Valencia' varieties on each sample date. Malathion (2EC) was applied at 1.5 g AI/ℓ with a hydraulic sprayer at 29 kg/cm^2 (ca 38 ℓ/tree). Three applications were made at 3-week intervals and samples were taken after the third application.

Samples were taken on days 1, 3, 5, 7, 14, and 21, frozen at -20°C and transported frozen to Lake Alfred for analysis. Samples were stored approximately 1 month at -10°C prior to analysis. Dual samples were taken on days 1, 3, 5, and 7. One set was washed in a weak soap solution (liquid Ivory^R) to simulate homeowner washing.

For analysis, fruit were thawed, the rind removed from one-half of each fruit, and the pulp sliced into a Waring blender. The pulp was blended for 3 min and a 10-g subsample removed for analysis. The rind was diced, blended for 3 min, and a 10-g subsample removed for analysis. The 10-g subsample of either rind or pulp was homogenized in 100 mℓ of methylene chloride and 15 g of sodium sulfate for 5 min in a Sorvall blending cup in an ice bath. The blender cup top was loosened upon removal and particulate matter allowed to settle for 1 min. A 20 mℓ aliquot was evaporated to dryness at 40° under N_2 and transferred to brown glass bottles over sodium sulfate in 10 mℓ of benzene. The mean $\pm$ S.D. for recoveries of malathion and malaoxon were 98 $\pm$ 3% and 94 $\pm$ 4%, respectively, from fortified pulp and rind homogenates. No varietal differences in recovery of standard materials were observed. Extractions were stored at -20°C prior to GLC analysis.

GLC analyses for malathion and malaoxon were performed on a Tracor 550 GLC with phosphorous flame photometric detection. Operating conditions were: 1.8 m x 2 mm I.D. glass column packed with 5% SP2100 on 100/120 mesh GCQ, N_2 60 mℓ/min, detector 200°, injection port 210°, oven 190°. Quantification was by comparison with the peak height of standard materials chromatographed at the same attenuation. Standards were chromatographed every fourth injection. All injections were 5 µℓ. One-hundred mℓ of each solvent was evaporated to 1 mℓ and 5 µℓ chromatographed to check for interfering materials. Standard malathion and malaoxon were provided by American Cyanamid Co., Princeton, NJ. The first-order time-based decay model used was:

$$\ln \frac{y}{y_o} = -\lambda t \qquad (1)$$

and the first-order time-weather based decay model was

$$\ln \frac{y}{y_o} = a_o \, dt + a_1 \, x_1 dt + \ldots\ldots + a_n \, x_n \, dt \qquad (2)$$

where y_o = initial pesticide residue, a = coefficient, $x_1 \ldots\ldots, x_n$ = environmental variables and t = ordinary time. Other statistics and computer programs have been described (Nigg et al., 1977a, 1978).

RESIDUE TECHNIQUE EXPERIMENT

Parathion (0,0-diethyl O-(4-nitrophenyl) phosphorothioate) was applied to 12-year-old 'Valencia' orange trees at 500 psi by hand to four-tree plots in a four replicate random block design. Treatments were: (1) parathion wettable powder (WP), (2) parathion emulsifiable concentrate (EC), and (3) no spray (NS). Rates are given in the appropriate tables in the Results section.

Leaves were vacuumed according to the method described by Popendorf et al. (1975). In these studies, the vacuum head was redesigned to improve sampling time and to allow use of the leaves for residue measurements after vacuuming. Sixty leaves, carefully picked by the petiole and inserted individually into the redesigned apparatus constitute a vacuum sample. After vacuuming, the filter was placed into a petri dish and the vacuum head and gaskets (except for the rubber gasket) rinsed with hexane into the dish. Filters were air-dried in the laboratory (ca 15 min), folded carefully and placed into 4-oz brown bottles. Each petri dish was rinsed twice with benzene into a 50 mℓ volumetric flask. The volumetric flask was brought to volume with benzene and benzene was added to the brown bottle. Mean $\pm$ S.D. extraction recoveries from dust fortified with parathion and paraoxon were 98 $\pm$ 3% for parathion and 92 $\pm$ 2% for paraoxon.

For vacuuming leaves, the following 90-mm filters were used: Millipore 0.8 μ with an efficiency of ca 100% in the 0.8 μ range (Megaw and Wiffen, 1963); Millipore 5.0 μ with an efficiency of 90+% (Liu and Lee, 1976) and a Whatman GF/A glass fiber filter, effective retention of 1.6 μ (Whatman catalog).

Forty leaves of each vacuum sample were punched immediately after vacuuming to be used with the Gunther et al. dislodgeable residue method (Iwata et al., 1977). An unvacuumed 40-leaf punch sample was also taken from each plot to obtain a total surface residue level as measured by the Gunther et al. method.

Particulate sizes were determined with a Millipore Model II MC particle measurement computer (Millipore Corp., Bedford, MA 01730) and for sizes > 5.0 μ with a reticle under 400X magnification with phase contrast. Values are averages of five lensfields per replicate. For particulate size analyses on aqueous samples obtained from the Gunther method and the aqueous spray tank samples, a Millipore 0.22 μ filter was used. The leaf area of both sides of each leaf was obtained by using the formula of Turrell (1961) and multiplying by two.

SMALL PLOT EXPERIMENT

Experimental design, application methodology, sampling extraction of

fruit, leaves and soil, and weather monitoring were previously described (Nigg et al., 1977a, 1978, 1979; page 4 this report). Dioxathion (8E) (2,3-p-dioxanedithion S,S-bis(0,0-diethyl) phosphorodithioate, oxydemeton-methyl (2L) (S-[2-(ethylsulfinyl) ethyl] 0,0-dimethyl phosphorothioate, dialifor (4E) (0,0-diethyl phosphorodithioate S-ester with N-(2-chloro-1-mercapto-ethyl) phthalimide, and malathion (9.5E) (0,0-dimethyl phosphoro-dithioate of diethyl mercaptosuccinate) were applied at a rate of 4 lbs AI/acre in 750 gal of water/acre (4.48 kg AI/ha in 285 dkl water). Both experiments were carried out on the same plots. Experiment 1 was conducted from March 14 to April 11, 1978 and Experiment 2 from July 11 to August 9, 1979.

Dioxathion, oxydemetonmethyl and dialifor were analyzed at 210°, 190° and 230°C, respectively on a 0.8 mx2 mm I.D. silanized glass column packed with 10% DC-200 + 1.5% QF-1 on 80/100 mesh Chromosorb W(HP). This packing material was a gift of Dr. J. S. Thornton, Mobay Chemical Corp., Kansas City, MO 64120. Detection was with a nitrogen-phosphorous detector in a Hewlett-Packard 5730A gas chromatograph. Other conditions were: He, 30 mℓ/min, injection port 250°, detector 200°. Malathion was analyzed on a 0.8 m x 2 mm I.D. silanized glass column packed with 5% SP2100 on 100/120 mesh GCQ. Operating conditions of the Tracor 550 GC were: column temp-erature 180°, injection port 210°, flame-photometric detector 180°, N_2 40 mℓ /min.

Extraction of leaf and fruit washes and soil were as previously described (page 4, this report). Oxydemetonmethyl was oxidized to the sulfone prior to gas chromatography according to the method of Thornton et al. (1977).

Analytical standards of dioxathion and dialifor were provided by Hercules, Inc., Wilmington, DE 19899. Malathion and malaoxon standards were provided by American Cyanamid Corp., Princeton, NJ and oxydemeton-methyl and oxydemetonmethyl sulfone were provided by Mobay Chemical Corp., Kansas City, MO 64120.

The mean $\pm$ S.D. for recoveries from fortified 40-leaf punch washes were: malathion 88.8 $\pm$ 2.4%; malaoxon 94.6 $\pm$ 4.5%; dialifor 83.9 $\pm$ 5.8%; oxydemetonmethyl 96.9 $\pm$ 2%; and dioxathion 80 $\pm$ 3.3%. Results are not corrected for recovery.

SECTION V

RESULTS AND DISCUSSION

LARGE PLOT PARATHION EXPERIMENT

Fruit and Leaf Residue

The weather model for parathion disappearance on 'Valencia' orange leaves and fruit is presented in Fig. 1. It should be noted in Tables 1 and 2 that the data trends for fruit and leaves and EC and WP formulations are not statistically different. The model of parathion disappearance in Fig. 1 utilized both EC and WP parathion residue averages of leaves and fruit residues. Time is not used in this model and cumulative rainfall (inches), cumulative solar incidence (cal/cm^2), cumulative leaf wetness (hrs.), and cumulative average temperature (C° days) account for 75.7% of the variation observed in the residue data. Time alone accounts for only 55% of the variation observed. Cumulative average temperature and heating degree days correlated equally well with parathion residues (Table 1). For this reason, cumulative average temperature was used in place of heating-degree-days since they are approximately proportional and the calculation of cumulative average temperature does not require a computer.

The weather model presented in Fig. 1 was the best overall model. No improvement in variation explained was obtained by including time instead of one of the environmental variables. In the overall fruit and leaf model, cumulative solar incidence appeared to be the most important environmental variable with an R = 0.828. The addition of rainfall yielded a multiple R of 0.851, cumulative average temperature a multiple R of 0.861, and cumulative leaf wetness a multiple R of 0.870.

On the other hand, the paraoxon-environmental variable correlations in Tables 3 and 4 indicate the importance of cumulative rainfall. This is similar to previous weather correlations of paraoxon residues in Florida citrus (Nigg et al., 1978). This result also supports the supposition that differences in the levels of paraoxon residues between Florida and California citrus are due to wet conditions in Florida and dry conditions in California (Gunther et al., 1977; Nigg et al., 1978). However, the reasons for paraoxon residue differences between geographical regions are blurred because of simultaneous paraoxon production from parathion and disappearance behavior of paraoxon itself. The environmental production and persistance of paraoxon apparently depends on dusty conditions, ozone, and dry weather (Popendorf and Leffingwell, 1978; Spear et al., 1975, 1978). The environmental dependence of paraoxon production on plant surfaces is

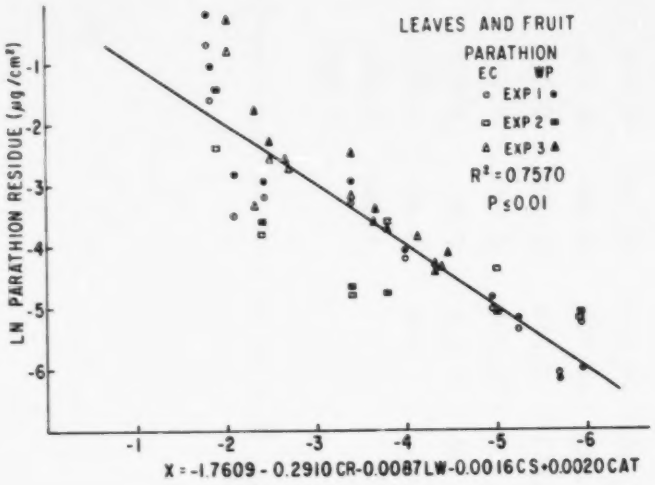

Figure 1. Weather model of emulsifiable concentrate (EC) and wettable powder (WP) parathion disappearance on 'Valencia' orange leaves and fruit. Residue values are the average of fruit and leaf residues in $\mu g/cm^2$. Each point is the average of eight replicates (four fruit, four leaf) CS = cumulative solar incidence, cal/cm^2 (cumulative daily hrs.), LW = cumulative leaf wetness (cumulative hrs.), CR = cumulative rainfall (inches), CAT = cumulative average temp. (C° days < 0).

an important consideration in prediction of safe worker reentry times (Spear, 1978). Once this dependence is known, accurate correlations of paraoxon disappearance and environmental factors can be made from field data as presented here.

The use of the Andersen mini-sampler for assessing airborne particulate matter dislodged during picking operations has been successful when worn by pickers (Westlake et al., 1973). No parathion, paraoxon, or dust were obtained by the sweeping techniques described here. It appears that it is necessary for a picker to wear the mini-sampler for at least 1 hr for a measurable sample.

Dust levels on leaf and fruit surfaces as determined gravimetrically did not vary significantly over the course of an experiment or between experiments. Dust levels averaged 105 $\mu g/cm^2$ (range 20-170 $\mu g/cm^2$) on leaf surfaces and 70 $\mu g/cm^2$ (range 44-96 $\mu g/cm^2$) on fruit surfaces. These dust levels are ca 1/3 of those reported by Popendorf et al. (1975) and these data

TABLE 1. SIMPLE CORRELATION MATRIX FOR WP PARATHION RESIDUES AND ENVIRONMENTAL VARIABLES

Leaves	Fruit	Soil-Mid.	Soil-Drip	Time[a]	HDD1[b]	HDD2[c]	CR[d]	CLW[e]	CS[f]	CAT[g]
1.000	0.905[h]	0.847	0.577	-0.625	-0.636	-0.579	-0.847	-0.637	-0.770	-0.646
	1.000	0.850	0.615	-0.774	-0.690	-0.536	-0.741	-0.742	-0.851	-0.761
		1.000	0.649	-0.666	-0.742	-0.704	-0.748	-0.742	-0.728	-0.696
			1.000	-0.642	-0.625	-0.526	-0.566	-0.665	-0.654	-0.618
				1.000	0.883	0.653	0.660	0.940	0.946	0.981
					1.000	0.931	0.755	0.985	0.806	0.945
						1.000	0.736	0.861	0.586	0.766
							1.000	0.719	0.721	0.715
								1.000	0.863	0.977
									1.000	0.923
										1.000

[a] Time in days.

[b] HDD1 temp. limits 0°, 37.8°C.

[c] HDD2 temp. limits 10°, 37.8°C.

[d] Cum. rainfall (inches).

[e] Cum. leaf wetness (h).

[f] Cum. solar incidence in cal cm^{-2}.

[g] Cum. avg. temp.

[h] When $R \geq 0.496$, $P \leq 0.01$.

TABLE 2. SIMPLE CORRELATIONS FOR EC PARATHION RESIDUES AND ENVIRONMENTAL VARIABLES

	Time[a]	HDD1[b]	HDD2[c]	CR[d]	CLW[e]	CS[f]	CAT[g]
Leaves	-0.604[h]	-0.601	-0.537	-0.789	-0.604	-0.725	-0.616
Fruit	-0.760	-0.652	-0.484	-0.694	-0.714	-0.837	-0.748
Soil-Mid.	-0.636	-0.777	-0.784	-0.811	-0.758	-0.688	-0.697
Soil-Drip	-0.280	-0.374	-0.390	-0.386	-0.360	-0.289	-0.321

[a]Time in days.

[b]HDD1 temp. limits 0°, 37.8° C.

[c]HDD2 temp. limits 10°, 37.8° C.

[d]Cum. rainfall (inches).

[e]Cum. leaf wetness (h).

[f]Cum. solar incidence in cal cm^{-2}.

[g]Cum. avg. temp.

[h]When $R \geq 0.496$, $P \leq 0.01$.

TABLE 3. SIMPLE CORRELATIONS FOR WP PARAOXON RESIDUES AND ENVIRONMENTAL VARIABLES

	Time[a]	HDD1[b]	HDD2[c]	CR[d]	CLW[e]	CS[f]	CAT[g]
Leaves	-0.504[h]	-0.659	-0.691	-0.708	-0.642	-0.546	-0.584
Fruit	-0.406	-0.595	-0.665	-0.803	-0.556	-0.435	-0.485
Soil-Mid.	-0.276	-0.479	-0.570	-0.530	-0.435	-0.280	-0.376
Soil-Drip	-0.485	-0.565	-0.548	-0.716	-0.549	-0.519	-0.534

[a]Time in days.

[b]HDD1 temp. limits 0°, 37.8° C.

[c]HDD2 temp. limits 10°, 37.8° C.

[d]Cum. rainfall (inches).

[e]Cum. leaf wetness (h).

[f]Cum. solar incidence in cal cm^{-2}.

[g]Cum. avg. temp.

[h]When $R \geq 0.496$, $P \leq 0.01$.

TABLE 4. SIMPLE CORRELATIONS FOR EC PARAOXON RESIDUES AND ENVIRONMENTAL VARIABLES

	Time[a]	HDD1[b]	HDD2[c]	CR[d]	CLW[e]	CS[f]	CAT[g]
Leaves	-0.529[h]	-0.585	-0.554	-0.772	-0.581	-0.559	-0.560
Fruit	-0.157	-0.176	-0.200	-0.574	-0.178	-0.342	-0.186
Soil-Mid.	-0.449	-0.557	-0.573	-0.671	-0.553	-0.461	-0.508
Soil-Drip.	-0.442	-0.433	-0.389	-0.637	-0.444	-0.448	-0.435

[a]Time in days.

[b]HDD1 temp. limits 0°, 37.8° C.

[c]HDD2 temp. limits 10°, 37.8° C.

[d]Cum. rainfall (inches).

[e]Cum. leaf wetness (h).

[f]Cum. solar incidence in cal cm^{-2}.

[g]Cum. avg. temp.

[h]When $R \geq 0.496$, $P \leq 0.01$.

indicate an additional difference in Florida and California conditions which may help explain the lack of reports of acute toxic effects for pickers exposed in Florida citrus. Differences between Florida and California regarding actual amounts of particulate matter dislodged during picking operations await elucidation.

Cover Crop Residues

Cover crop residues were obtained during experiment 1 (Jan. - Mar. 1977) after having allowed the native weed and grasses unrestricted growth from Aug. 1976 to Jan. 1977. The disappearance of the residue from the cover crop was more rapid than from any other sample. Cover crop residues of WP parathion were about 12.0 ppm on day 1, 1.3 ppm on day 3, and 0.2 ppm on day 7. Residues of EC parathion on the cover crop were about 4.0 ppm on day 1, 0.70 ppm on day 3, and 0.15 ppm on day 7. No residues of either EC or WP parathion were detected after day 7 post application. The half-life of parathion on the cover crop was about 1 day compared to 1.3 days for air and 2.0 days for fruit, leaves, and soil surface. I attribute this observation to increased hours of foliage wetness as dew condenses from the ground up and disappears from the top down. The cover crop was observed to remain wet long after the tree foliage was dry.

The speculation that fruit pickers and grove workers might be exposed to residues on the cover crop is not supported by our residue data nor by normal grove practice. Florida citrus groves are regularly disced and mowed before picking operations at the demand of pickers to reduce inconvenience and the possibility of rattlesnake bite.

Soil Surface Residues

Parathion disappearance from the soil surface between trees, although slightly slower, is essentially at the same rate as for leaves and fruit. There was no significant difference in the rate of decay between EC and WP formulations on the soil surface and these data are combined in Fig. 2. The overall weather model and simple correlations indicate that cumulative rainfall may be important to disappearance of parathion on the soil surface between trees in Florida (Tables 1, 2, and 5). The weather model accounts for about 78% of the soil surface parathion residue data between trees whereas time alone explains only 42% on the data variation.

Paraoxon residue behavior on the soil surface between trees showed the strongest correlation with cumulative rainfall (-0.530 for WP and -0.671 for EC) suggesting the importance of hydrolysis or water solubility for the disappearance of paraoxon. Compared to leaf surface paraoxon correlations, however, both the simple and multiple correlations for paraoxon behavior on the soil surface were poor (Tables 3, 4, and 5).

Soil surface residue data for parathion disappearance at the dripline of the tree did not fit first-order kinetics for EC parathion, but were approximately first-order for WP parathion (Table 5). The overall model for WP parathion at the tree dripline does not show the dependence on rainfall that was observed with the soil residue between trees. Differences in the solar and temperature processes at the dripline and nonuniform foliage channeling of residue runoff at application and during rainstorms might account for this observation.

Residues in Ambient Air

The ambient air parathion data in Fig. 3 show levels of about 5.0, 2.5, 0.5, and 0.1 $\mu g/m^3$ of parathion 1, 3, 6, and 8 days post-treatment in experiments 2 and 3. There was no difference between WP and EC formulations nor between experiments for parathion levels in air. The very low air levels of parathion in the no-spray plots indicate that the 0.75-acre (0.3 ha) plot size used in these experiments may be adequate for determination of pesticides in air. No paraoxon was detected in any air sample.

Total Residues

Since values did not differ between experiments, the average percent total residue was used in Fig. 4. It is readily apparent in Fig. 4 that the leaf surface residue represents the greatest potential for worker exposure. For parathion, the soil surface contained half as much compared to leaf surface of the total plot residue hazardous to workers, while fruit and ambient air contained negligible percentages of residue available to workers.

TABLE 5. MULTIPLE LINEAR REGRESSION[a] OF PARATHION AND PARAOXON RESIDUES AND ENVIRONMENTAL VARIABLES

	R^2 x 100	Ln initial conc.	Coefficients A_1	A_2	A_3	A_4
EC Parathion						
Leaves	72.7	-1.9764	-0.7912	-0.0065	0.0024	-0.0070
Fruit	72.6	-2.2522	-0.1282	-0.0046	0.0010	-0.0041
Soil-Mid.	79.1	2.3005	-0.6386	-0.0045	0.0046	-0.0305
Soil-Dripline	18.3	1.5237	-0.4953	--	0.0020	-0.0175
EC Paraoxon						
Leaves	60.0	-4.9967	-1.1123	--	--	--
Fruit	55.1	-5.6513	-1.0834	-0.0041	0.0020	0.0004
Soil-Mid.	48.3	-1.9429	-1.6476	--	0.0033	-0.0265
Soil-Dripline	41.0	-3.5277	-1.7148	--	0.0004	--
WP Parathion						
Leaves	85.3	-1.1538	-0.9763	-0.0093	0.0041	-0.01483
Fruit	78.7	-1.6067	-0.2304	-0.0057	0.0019	-0.0091
Soil-Mid.	77.5	2.6433	-0.4415	-0.0075	0.0057	-0.0349
Soil-Dripline	61.6	2.7685	-0.0310	-0.0133	0.0095	-0.0591
WP Paraoxon						
Leaves	57.8	-4.9641	-0.6760	-0.0017	0.0030	-0.0227
Fruit	74.3	-4.0270	-1.4043	0.0012	0.0026	-0.0181
Soil-Mid.	36.3	-1.8490	-1.8246	0.0091	--	-0.0170
Soil-Dripline	51.2	-1.8935	-1.9019	--	--	--

[a]Residue = Ln initial conc. + A_1 (cum. rain in.) + A_2 (cum. solar, h) + A_3 (cum. avg. temp.) + A_4 (cum. leaf wet, h).

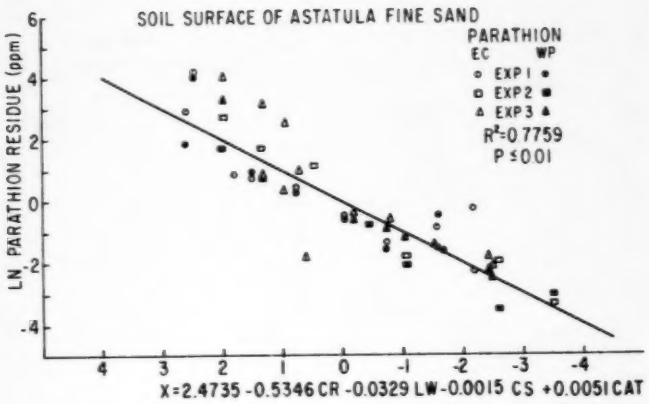

Figure 2. Weather model of emulsifiable concentrate (EC) and wettable powder (WP) parathion disappearance on the soil surface of Astatula fine sand between trees. Each point is the average of four replicates. CS = cumulative solar incidence, cal/cm^2 (cumulative daily hrs.), LW = cumulative leaf wetness (cumulative hrs.), CR = cumulative rainfall (inches), CAT = cumulative average temp. (C° days <0).

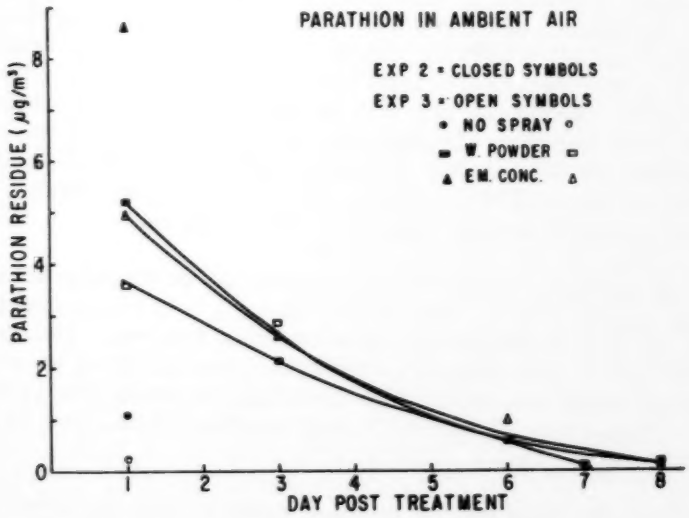

Figure 3. Parathion in ambient air in μg/m^3.

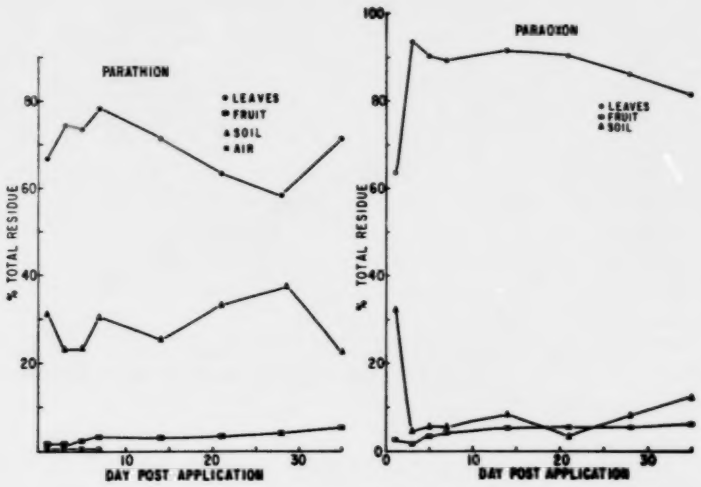

Figure 4. Percentage of parathion and paraoxon residues in air, on 'Valencia' orange leaves, on 'Valencia' orange fruit, and on the soil surface.

The leaf surface generally contained 90% whereas the soil and fruit contained about 10% each of the paraoxon residues. These results are in substantial agreement with Westlake et al. (1973), Gunther et al. (1973), and Leffingwell et al. (1975). Based on these results, leaf surface and soil surface residue determinations may be sufficient to assess residue levels of pesticidal chemicals for the protection of farmworkers. Respiratory exposure from ambient air and exposure to the hands in picking operations would appear to be not significant, agreeing with Gunther et al. (1973) and Wolfe et al. (1975). These type of data may become useful when correlations with actual worker exposure are observed.

If accurately constructed, models of pesticide behavior should have worldwide application. While the slope coefficient multiplying the weather variable in the multiple regression equation must remain constant, the variable itself may vary greatly from time to time or region to region. This can produce the effect of altering or even completely reversing the relative "importance" of different weather variables in different regions or at different times.

Monitoring studies of residue dissipation on plant parts and on the soil surface are currently required for the registration of pesticides. Methods for estimating worker reentry times both mathematically (Serat, 1973, 1974, 1978; Serat et al., 1975) and with laboratory animals (Guthrie et al., 1974) have been suggested. The weather model of parathion disappearance presented here indicates that the estimation of residues on plant parts, which is critical for the mathematical approach, can be done accurately. This accuracy, however, can probably be improved by investigation of the

importance of individual processes to pesticide disappearance from plant parts, i.e., hydrolysis, volatilization, photolysis, etc.

MALATHION FRUIT EXPERIMENT

Malaoxon was not found in any sample. Only uninterpretable traces of malathion were detected in pulp. This lack of malathion in citrus pulp agrees with the results of Blinn et al. (1959). There was no difference ($P > 0.05$) between washed and unwashed fruit rind residues and these data were combined for statistical purposes. The lack of a measurable difference between these paired samples could have been due to sample handling.

The disappearance of malathion on and in the rind of each variety tended to show exponential decay (a first-order process) (Fig. 5), except for lemon which showed a poor correlation of -.50 (Table 6). The half-life of malathion was about 8 days for all varieties (Table 6). This agrees with half-life of 7 days for malathion degradation behavior on and in California 'Valencia' orange calculated from 1 to 14 days post application data ($R = 0.98$) (Blinn et al., 1959). They reported a persistence behavior half-life of 32 days for malathion calculated from 21 to 62 day post application data. Using Blinn et al. (1959) overall 1 to 62 day data, a 13.9 day half-life is obtained ($R = -0.92$) which would indicate that malathion is about one-half as persistent in Florida fruit compared to California fruit.

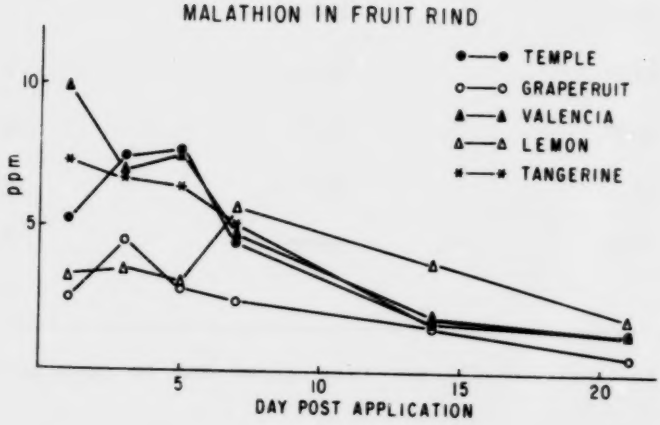

Figure 5. Malathion disappearance in the rind of Florida citrus varieties. Points for days 1 to 7 are averages of eight determinations while 14 and 21 day points are averages of four determinations.

Malathion residues reached a level of 8 ppm or less in the rind of Florida citrus within 5 days after application during the relatively dry, cool Florida winter (Nov. - Jan., 1976-77) (avg. temp. in Ft. Lauderdale: Nov. 1976, 21.5°C; Dec. 1976, 19.6°C; Jan. 1977, 15.5°C). Previous organophosphate residue data indicate that malathion residue levels < 8 ppm would

be reached in about 3 days for rind and less than 12 hrs. for pulp under relatively wet summer conditions (Nigg et al., 1977a, 1978).

Time-based half-life differences appear to be related to differences in weather (Nigg et al., 1977a, b, 1978). The use of time plus weather is more accurate for modeling malathion residue decay compared to time alone (Tables 6, 7). For example, the correlation of the lemon data is significantly improved from an R of -.50 (time alone) to -.88 by modifying the first-order model base to include weather (Table 6). As noted by Nigg et al. (1978), a variety of weather sets is necessary to demonstrate significant differences between a time model and a time-weather model of first-order pesticide disappearance. Previous weather models for the disappearance of pesticides from leaf surfaces were highly accurate (Nigg et al., 1977a, 1978), and this approach has been suggested for preharvest intervals in food commodities (Nigg et al., 1978). These fruit rind data for malathion indicate that the use of physical factors to predict the residue level on foodstuffs is a viable scientific approach.

TABLE 6. MALATHION FIRST-ORDER RESIDUE BEHAVIOR IN FLORIDA CITRUS VARIETIES BASED ON TIME ALONE AND TIME PLUS WEATHER

Variety	% variation explained (r^2 x 100)[a]		t 1/2 (days)
	Time alone	Time + HDD + Cum. rainfall	
Temple	78*	86**	7.7
Grapefruit	81**	93**	7.7
Valencia	96**	98**	6.9
Lemon	25	78*	8.7[b]
Tangerine	94**	98**	7.7
$\bar{X}$			7.7

[a] r = correlation to equation (1) for time alone and to equation (2) for time and weather.

[b] t 1/2 based on 7, 14 + 21 day data.

*P < 0.05 (Morrison, 1967).

**P < 0.01.

TABLE 7. VARIABLES USED AS BASE FOR FIRST-ORDER MODEL OF MALATHION RESIDUE DISAPPEARANCE

Day post treatment	1	3	5	7	14	21
Variable						
Cum. time (days)	1	3	5	7	14	21
Cum. heating-degree days	15	30	41	59	157	294
Cum. rainfall (inches)	.63	.64	.64	.64	.73	.82

RESIDUE TECHNIQUE EXPERIMENT

The redesigned vacuum head and the use of Turrell's formula allowed two significant improvements in the foliage vacuum method. Spray painting leaves to obtain a leaf area estimate was eliminated so the leaves were available for further residue analysis. Both sides of a leaf were vacuumed at once which reduces the previous 25 min sampling time to 10 min.

There was no significant difference between the 0.8 μ and 5.0 μ filters in the amount of pesticide removed or in the overall trend of both parathion and paraoxon disappearance (r = 0.992) (Table 8). The 5.0 μ filter and the glass fiber filters were also highly correlated with one another in the overall trend of the parathion and paraoxon data (r = 0.959) (Table 9), but the glass fiber filter differed significantly (5% level or better) from the 5.0 μ filter in the amount of WP parathion removed on days 1, 2, and 5 and in the amount of paraoxon on days 1 and 9. These residue collection differences appear to be related to air flow rate (Table 10) and reach significance (5% level or better) with the comparison of the glass fiber and 5.0 μ filters (Table 9). The flow rate of the glass fiber filter is 5,000 fpm compared to 2,250 with the 5.0 μ filter. Comparison of the means without regard to variation showed an approximate doubling of pesticide residue collected with the glass fiber filter. Similar trends were evident with the 0.8 μ filter and 5.0 μ filter comparison (Table 8). The 0.8 μ filter had a dustless flow rate of 1,600 fpm vs. 2,250 for the 5.0 μ filter, apparently not enough difference to reach statistical significance in the amount of pesticide removed. The absolute amount of residue may be less important than consistent data for researchers working in dusty groves. The experiments reported here reflect dust levels on foliage too low for gravimetric analyses, but with dusty conditions the 5.0 μ filter showed the least flow rate change with increasing dust load and may produce the most consistent data (Table 10).

The correlation of the EC and WP vacuum data in Table 11 for both paraoxon and parathion was 0.982. There was significantly less vacuumable EC pesticide compared to WP pesticide on day 1, 3, and 8 for both parathion

TABLE 8. EXPERIMENT 1 (MARCH 24-31, 1977): COMPARISON OF 0.8 μ and 5.0 μ FILTERS WITH PARATHION WP (3 LB 25 WP/100 GAL) ($\mu g/cm^2$)

Treatment	Day 1 post application			Day 6 post application		
	Po (Paraoxon)	Pt (Parathion)	Po/Pt	Po	Pt	Po/Pt
0.8 μ filter						
Vacuum	0.004 ± 0.001[a]	0.018 ± 0.004	0.25	0.002 ± 0.001	0.004 ± 0.001	0.62
Vacuum punch	0.080 ± 0.014	1.030 ± 0.326	0.08	0.028 ± 0.013	0.015 ± 0.009	1.92
Total (vac. + vac. punch)	0.084 ± 0.013	1.046 ± 0.324	0.08	0.030 ± 0.014	0.018 ± 0.010	1.49
Vacuum/total ratio	0.05	0.02	--	0.07	0.19	--
5.0 μ filter						
Vacuum	0.005 ± 0.001	0.027 ± 0.012	0.18	0.004 ± 0.001	0.004 ± 0.001	0.99
Vacuum punch	0.076 ± 0.007	1.009 ± 0.137	0.08	0.034 ± 0.011	0.014 ± 0.002	2.44
Total (vac. + vac. punch)	0.081 ± 0.008	1.036 ± 0.141	0.08	0.038 ± 0.011	0.018 ± 0.003	1.88
Vacuum/total ratio	0.06	0.03	--	0.11	0.24	--
Dislodgeable	0.060 ± 0.010	1.039 ± 0.256	0.06	0.028 ± 0.012	0.013 ± 0.003	2.14

[a]Results expressed as mean ± S.D. (four replications).

(CONTINUED)

TABLE 8. (CONTINUED)

Treatment	Day 8 post application Po (Paraoxon)	Pt (Parathion)	Po/Pt
0.8 μ filter			
Vacuum	0.003 ± 0.001	0.002 ± 0.0002	2.19
Vacuum punch	0.014 ± 0.005	0.007 ± 0.004	2.12
Total (vac. + vac. punch)	0.017 ± 0.005	0.008 ± 0.004	2.13
Vacuum/total ratio	0.20	0.20	--
5.0 μ filter			
Vacuum	0.004 ± 0.001	0.004 ± 0.002	1.03
Vacuum punch	0.029 ± 0.004	0.009 ± 0.002	3.25
Total (vac. + vac. punch)	0.032 ± 0.005	0.012 ± 0.004	2.22
Vacuum/total ratio	0.10	0.29	--
Dislodgeable	0.020 ± 0.007	0.006 ± 0.003	3.16

TABLE 9. EXPERIMENT 2 (APRIL 7-15, 1977): COMPARISON OF 5.0 μ AND GLASS FIBER FILTERS WITH PARATHION WP (3 LB 25 WP/100 GAL) (μg/cm^2)

Treatment	Day 1 post application			Day 2 post application		
	Po (Paraoxon)	Pt (Parathion)	Po/Pt	Po	Pt	Po/Pt
5.0 μ filter						
Vacuum	0.005 ± 0.001[a]	0.067 ± 0.030	0.07	0.005 ± 0.002	0.022 ± 0.011	0.23
Vacuum punch	0.028 ± 0.015	1.671 ± 0.553	0.02	0.066 ± 0.008	0.730 ± 0.048	0.09
Total (vac. + vac. punch)	0.033 ± 0.016	1.738 ± 0.579	0.02	0.071 ± 0.009	0.752 ± 0.053	0.09
Vacuum/total ratio	0.15	0.04		0.07	0.03	
Glass filter						
Vacuum	0.07 ± 0.0002	0.198 ± 0.044	0.04	0.008 ± 0.001	0.123 ± 0.016	0.07
Vacuum punch	0.075 ± 0.015	2.630 ± 0.076	0.03	0.066 ± 0.009	0.801 ± 0.106	0.08
Total (vac. + vac. punch)	0.082 ± 0.015	2.828 ± 0.049	0.03	0.073 ± 0.008	0.924 ± 0.105	0.08
Vacuum/total ratio	0.09	0.07		0.11	0.13	
Dislodgeable	0.037 ± 0.014	1.812 ± 0.487	0.02	0.103 ± 0.013	1.074 ± 0.096	0.10

[a]Results expressed as mean ± S.D. (four replicates).

(CONTINUED)

TABLE 9. (CONTINUED)

Treatment	Day 5 post application			Day 7 post application		
	Po (Paraoxon)	Pt (Parathion)	Po/Pt	Po	Pt	Po/Pt
5.0 μ filter						
Vacuum	0.003 ± 0.001	0.006 ± 0.002	0.50	0.002 ± 0.001	0.003 ± 0.002	0.67
Vacuum punch	0.034 ± 0.012	0.037 ± 0.017	0.92	0.028 ± 0.006	0.019 ± 0.007	1.47
Total (vac. + vac. punch)	0.037 ± 0.014	0.043 ± 0.018	0.86	0.031 ± 0.005	0.022 ± 0.006	1.41
Vacuum/total ratio	0.08	0.14		0.06	0.14	
Glass filter						
Vacuum	0.005 ± 0.001	0.011 ± 0.002	0.45	0.003 ± 0.002	0.005 ± 0.004	0.60
Vacuum punch	0.051 ± 0.011	0.123 ± 0.047	0.41	0.028 ± 0.005	0.025 ± 0.006	1.12
Total (vac. + vac. punch)	0.057 ± 0.011	0.134 ± 0.046	0.43	0.031 ± 0.004	0.031 ± 0.007	1.00
Vacuum/total ratio	0.09	0.08		0.10	0.16	
Dislodgeable	0.050 ± 0.017	0.083 ± 0.039	0.60	0.023 ± 0.005	0.023 ± 0.012	1.00

(CONTINUED)

TABLE 9. (CONTINUED)

Treatment	Day 9 post application Po (Paraoxon)	Pt (Parathion)	Po/Pt
5.0 μ filter			
Vacuum	0.001 ± 0.0004	0.001 ± 0.0003	1.00
Vacuum punch	0.013 ± 0.001	0.007 ± 0.002	1.86
Total (vac. + vac. punch)	0.014 ± 0.002	0.008 ± 0.002	1.75
Vacuum/total ratio	0.07	0.13	
Glass filter			
Vacuum	0.002 ± 0.0003	0.002 ± 0.001	1.00
Vacuum punch	0.012 ± 0.003	0.010 ± 0.002	1.20
Total (vac. + vac. punch)	0.013 ± 0.002	0.013 ± 0.002	1.00
Vacuum/total ratio	0.15	0.15	
Dislodgeable	0.015 ± 0.006	0.008 ± 0.006	1.88

TABLE 10. FILTER FLOW CHARACTERISTICS

Filter	Flow (fpm)[a]				% change[b]		
	No load	25% load	75% load	100% load	25% load	75% load	100% load
0.8 μ	1600	1450	1325	1300	9.4,	17.2,	18.8
5.0 μ	2250	2250	2100	2000	0.0,	6.7,	11.1
Glass	5000	4800	4400	3500	4.0,	12.0,	30.0
Composite	1000	900	850	750	10.0,	15.0,	25.0

[a]Flow rates were measured with an Alnor 6060-P velometer at the slit face. 100% load equals 100 μg dust/cm^2 based on an average total leaf area of 2650 cm^2 for 10 samples of 60 'Valencia' orange leaves. According to Popendorf et al. (1975) 100 μg dust/cm^2 was the maximum level removed from leaves in California in 1973. Graphite was used as "dust."

[b]Percent decrease in flow from the no load situation.

and paraoxon and also for parathion on day 6. Comparing the EC dislodgeable and WP dislodgeable data in Table 11 showed significantly more pesticide removed with the WP formulation on days 3, 6, and 8. These observations are consistent with the fact that the WP formulation is a particulate formulation and these techniques are designed for particulates. Insofar as the dislodgeable residue technique and vacuum residue technique relate to fieldworker exposure, the EC formulation appears safer where the potential for attachment to environmental particulates is low.

Vaporization of pesticides from particulates in a high air flow and inefficient trapping of particulates are serious questions with the vacuum method and could result in loss of residue for analysis (Miles et al., 1970; Van Dyk and Visweswariah, 1975). The total (vacuum + vacuum punch) in Tables 8, 9, and 11 would be significantly smaller than the unvacuumed dislodgeable total residue if this were the case. There was no significant difference between these two totals. Consequently, under the conditions of these experiments, there was efficient trapping of particulate matter with residues attached and no measurable loss of parathion or paraoxon occurred due to the high air flow.

There was a possibility that vacuum determinations would have contained more paraoxon in relation to parathion as compared with the dislodgeable technique (Iwata et al., 1977), particularly since soils with smaller particulates can contain higher levels of paraoxon (Adams et al., 1976). Higher paraoxon-parathion ratios for the vacuum determinations might then indicate a special character of the residue substrate removed in relationship to paraoxon. This is the result on day 1 post application (Tables 8, 9, 11). On every other sampling day, both the vacuum punch (which is processed with the dislodgeable technique) and the dislodgeable total residue paraoxon-parathion ratio is equal to or greater than the vacuum sample. Thus, the dislodgeable residue technique fairly assesses the oxon metabolite level. No explanation is offered for the day 1 post application result.

Correlations of the data trends of the vacuum residue data with the Gunther et al. dislodgeable residue technique were 0.756 for paraoxon and 0.994 for parathion with the 0.8 μ filter and are 0.982 for paraoxon and 0.999 for parathion with the 5.0 μ filter. The EC vacuum data in Table 9 for both the 5.0 μ filter and the glass fiber filter also correlated significantly (5% level or better) with the EC dislodgeable residue data: 5.0 μ filter, 0.729 for paraoxon, and 0.959 for parathion; glass fiber filter 0.824 for paraoxon and 0.999 for parathion. The WP vacuum and WP dislodgeable data in Table 10 have a correlation of 0.936 for paraoxon and 0.980 for parathion. The EC vacuum and EC dislodgeable data have a correlation of -0.230 for paraoxon and 0.946 for parathion (Table 10). The negative correlation for paraoxon with the EC formulation is probably due to no decrease in EC vacuum paraoxon on day 3 and an apparent increase on day 6. These high correlations obtained comparing the vacuum and dislodgeable techniques are in substantial agreement with the results of Spear et al. (1977).

Overall, the particulate analyses showed that the Gunther et al. dislodgeable method removes approximately five times the number of particulates

TABLE 11. EXPERIMENT 3 (APRIL 27-MAY 4, 1977): COMPARISON OF WP AND EC FORMULATIONS OF PARATHION ($\mu g/cm^2$)

Treatment	Day 1 post application			Day 3 post application		
	Po (Paraoxon)	Pt (Parathion)	Po/Pt	Po	Pt	Po/Pt
EC (Emulsifiable Concentrate) 32 oz 4E/100 gal						
EC vacuum	0.001 ± 0.0005[a]	0.002 ± 0.0003	0.05	0.0001 ± 0	0.001 ± 0.0006	0.10
EC vacuum punch	0.023 ± 0.003	1.111 ± 0.078	0.02	0.009 ± 0.0004	0.081 ± 0.021	0.10
Total (vac. + vac. punch)	0.023 ± 0.003	1.113 ± 0.078	0.02	0.009 ± 0.0002	0.083 ± 0.021	0.11
Vacuum/total ratio	0.004	0.002	--	0.01	0.01	--
EC dislodgeable	0.026 ± 0.002	1.122 ± 0.222	0.02	0.008 ± 0.002	0.093 ± 0.042	0.09
WP (Wettable Powder) 5 lb 15 WP/100 gal						
WP vacuum	0.001 ± 0.0002	0.016 ± 0.004	0.06	0.0006 ± 0.0003	0.006 ± 0.002	0.10
WP vacuum punch	0.030 ± 0.002	1.142 ± 0.161	0.03	0.019 ± 0.004	0.260 ± 0.041	0.07
Total (vac. + vac. punch)	0.031 ± 0.002	1.158 ± 0.164	0.03	0.019 ± 0.004	0.266 ± 0.042	0.07
Vacuum/total ratio	0.03	0.01	--	0.03	0.02	--
WP dislodgeable	0.031 ± 0.008	1.647 ± 0.600	0.02	0.017 ± 0.004	0.243 ± 0.054	0.07

[a]Results expressed as mean ± S.D. (four replicates).

(CONTINUED)

TABLE 11. (CONTINUED)

Treatment	Day 6 post application			Day 8 post application		
	Po (Paraoxon)	Pt (Parathion)	Po/Pt	Po	Pt	Po/Pt
EC (Emulsifiable Concentrate) 32 oz 4E/100 gal						
EC vacuum	0.0003 ± 0.0004	0.0004 ± 0.0001	0.75	0.00004 ± 0.00001	0.0003 ± 0.00005	0.13
EC vacuum punch	0.004 ± 0.001	0.008 ± 0.0003	0.50	0.0003 ± 0.0001	0.002 ± 0.0003	0.15
Total (vac. + vac. punch)	0.004 ± 0.001	0.008 ± 0.0004	0.50	0.0003 ± 0.00005	0.002 ± 0.0003	0.15
Vacuum/total ratio	0.08	0.05	--	0.13	0.15	--
EC dislodgeable	0.002 ± 0.0005	0.006 ± 0.002	0.33	0.0006 ± 0.0001	0.0003 ± 0.0004	2.00
WP (Wettable Powder) 5 lb 15 WP/100 gal						
WP vacuum	0.0005 ± 0.0006	0.002 ± 0.0005	0.25	0.0002 ± 0.00008	0.0008 ± 0.0001	0.25
WP vacuum punch	0.008 ± 0.002	0.024 ± 0.004	0.30	0.003 ± 0.0008	0.012 ± 0.007	0.25
Total (vac. + vac. punch)	0.008 ± 0.002	0.026 ± 0.004	0.31	0.004 ± 0.0007	0.013 ± 0.006	0.31
Vacuum/total ratio	0.06	0.08	--	0.05	0.06	--
WP dislodgeable	0.005 ± 0.0005	0.025 ± 0.010	0.20	0.004 ± 0.0007	0.018 ± 0.008	0.22

TABLE 12. VACUUMED PARTICULATES SIZE ANALYSES 0.8 μ FILTER--DAY 1 POST APPLICATION (5-200 μ)

Sample	Total[a] avg. particles	5-10	10-15	15-20	20-25	25-30	30-35	35-40	40-45	>45	Mean particle size	<5 μ
60 leaves--EC	12.4	0	0	0.6	2.8	3.2	1.0	0.6	0.6	1.0	27.0	20
%[b]	79.0	0	0	4.8	22.6	25.8	8.1	4.8	4.8	8.1		
60 leaves--WP	93.6	0.4	0	1.8	27.8	25.8	6.8	9.0	8.0	4.4	27.0	20
%	89.7	0.4	0	1.9	29.7	27.6	7.3	9.6	8.5	4.7		
60 leaves--NS	41.6	1.0	1.2	5.0	10.4	7.0	2.6	2.2	1.6	1.8	23.6	20
%	78.8	2.4	2.9	12.0	25.0	16.8	6.3	5.3	3.8	4.3		

[a]Total avg. particles = total avg. particles > 5 μ per lensfield.

[b]% = % of total in size range 5-200 μ.

Note: Mean particle size does not include particles <5 μ.

TABLE 13. VACUUMED PARTICULATES SIZE ANALYSES 5.0 μ FILTER--DAY 1 POST APPLICATION (5-200 μ)

Sample	Total[a] avg. particles	5-10	10-15	15-20	20-25	25-30	30-35	35-40	40-45	>45	Mean particle size	<5 μ
60 leaves--EC	19.8	0.4	0.4	0.6	7.0	4.2	1.4	1.4	0.8	1.2	25.1	32
%[b]	87.9	2.0	2.0	3.0	35.4	21.2	7.1	7.1	4.0	6.1		
60 leaves--WP	56.6	0	0.4	1.8	21.0	15.8	4.4	3.2	5.0	1.6	25.6	48
%	94.1	0	0.7	3.2	37.1	28.0	7.8	5.7	8.8	2.8		
60 leaves--NS	36.8	0	0	1.0	14.8	7.0	2.4	2.8	2.2	1.6	25.7	20
%	86.3	0	0	2.7	40.2	19.0	6.5	7.6	6.0	4.3		
Air sample[c]	5.8	0.2	1.0	0.2	0.4	1.2	1.6	0.8	0.2	0.2	27.4	28
%	100.0	3.4	17.2	3.4	6.9	20.7	27.6	13.8	3.4	3.4		

[a]Total avg. particles = total avg. particles > 5 μ per lensfield.

[b]% = % of total in size range 5-200 μ.

[c]15 min air samples in experimental grove.

Note: Mean particle size does not include particles < 5 μ.

compared to the vacuum method. This agrees with the six times dislodgeable/vacuum comparison by particulate weight in a California study (Popendorf et al., 1975). For the 0.8 μ filter the EC formulation had an average of 12 particles (5-200 μ) per lensfield. This was 79% of the total particulate sample. The mean particle size was 27 μ. No-spray (NS) values were 42, 79%, and 24 μ respectively and the WP values were 94, 90%, and 27 μ respectively (Table 12).

With the 5.0 μ filter the EC formulation had 20 particulates (5-200 μ) per lensfield representing 88% of the total sample, with a mean particle size of 25 μ. The NS values were 37 particles per lensfield 5-200 μ in size representing 86% of the total sample and a mean particle size of 26 μ. The WP formulation values were 57, 94%, and 26 μ. Values for the air samples taken in the grove were six particulates (5-45 μ) which was 100% of the sample with a mean particle size of 27 μ. All of the above samples had about 25 particles < 5 μ per lensfield (Table 13). No particulate analyses were performed on the Whatman GF/A glass fiber filter.

Analyses of the particulate sizes and number using a 0.22 μ filter and the dislodgeable samples resulted in the following: EC, 260, 88%, 26 μ; NS, 240, 87%, 24 μ; WP, 264, 74%, 29 μ; WP tank sample diluted 1:100, 418, 60%, 23 μ; EC tank sample diluted 1:100, 16, 100%, 23 μ, and the grove soil passing 100 mesh, 125 particles representing 99% of the sample with a mean particle size of 39 μ. The above samples contained approximately 400 particles < 5 μ per lensfield except for the EC tank sample with 20 particles < 5 μ per lensfield (Table 14).

The relative numbers of particle sizes from 5 to 45 in 5 μ increments for the vacuum and dislodgeable techniques were the same. However, the vacuum technique recovered about 5 to 10% particulates < 5 μ when compared with the air and dislodgeable samples. Recent reports stress the importance of < 1 μ particulates in urban aerosols (Natusch and Wallace, 1974) and of 1.5 μ in aerosols with a soil derived component (Patterson and Gillette, 1977b).

All samples in this study were almost devoid of particulates in the 5 to 10 μ range and most had no particulates in the 10 to 15 μ range. In addition, only 5% of the particulate matter from the leaf was in the range of 45 to 200 μ. None of the air samples contained particulates above 45 μ. Thus, the major particulate load is < 45 μ on leaves and in air. Others report airborne particulate size ranges of < 50 μ (Patterson et al., 1976; Patterson and Gillette, 1977a, b) and these observations are consistent with an airborne transfer of soil particulates to the leaf surface. However, these data differ from airborne particulate sizes for three California citrus foliage samples which were reported to average 3.1 μ (Popendorf and Spear, 1974). Analyses of California soils report 5 to 43% (most over 10%) particulates < 2 μ and of 28 to 57% particulates from 2 to 50 μ (Adams et al., 1976; Iwata et al., 1973; Iwata et al., 1975). Analyses of 16 Florida citrus soils are strikingly different. Florida citrus soils are all classed as sands with 4.4 $\pm$ 2.8% 2 to 50 μ particulates and 1.8 $\pm$ 0.9% < 2 μ particulates (Table 15). From these soil data it appears that the "potential"

TABLE 14. FILTERED AQUEOUS SAMPLES PARTICULATE SIZE ANALYSES (0.22 μ)--DAY 1 POST APPLICATION (5-200 μ)

Sample	Total[a] avg. particles	5-10	10-15	15-20	20-25	25-30	30-35	35-40	40-45	>45	Mean particle size	< 5 μ
10 leaves--EC	260.2	0	0	9.0	82.8	63.2	21.0	23.6	16.0	12.0	26.4	400
%[b]	87.5	0	0	3.5	31.8	24.3	8.1	9.1	6.1	4.6		
10 leaves--WP	264.2	0.4	0.8	2.6	45.2	59.0	33.6	26.4	29.2	22.4	29.1	400
%	74.2	0.2	0.3	1.0	17.1	22.3	12.7	1.0	11.1	8.5		
10 leaves--NS	240.4	0.2	1.6	37.4	77.4	43.2	18.0	13.0	10.2	7.8	23.7	400
%	86.9	0.1	0.7	15.6	32.2	18.0	7.5	5.4	4.2	3.2		
Tank sample... 15 WP dil. 1:100	417.8	0.6	0.4	9.4	35.4	50.6	39.2	35.2	38.8	39.6	23.1	400
%	59.6	0.1	0.1	2.2	8.5	12.1	9.4	8.4	9.3	9.5		
Tank sample... 4E (EC) 1:100	16.0	0	0.4	0.2	2.4	2.8	1.4	1.8	1.6	1.2	23.4	20
%	100.0	0	2.5	1.3	15.0	17.5	8.8	11.3	10.0	7.5		
Astatula fine sand passing 100 mesh	124.8	0	0	1.0	8.8	13.3	10.8	9.0	14.0	66.3	38.9	400
%	98.8	0	0	0.8	7.1	10.7	8.7	7.2	11.2	53.1		

[a]Total avg. particles = total avg. particles > 5 μ per lensfield.

[b]% = % of total in size range 5-200 μ.

Note: Mean particle size does not include particles < 5 μ.

TABLE 15. SOIL PARTICULATE DISTRIBUTION IN FLORIDA CITRUS SOILS (% <2 μ in 0-7" HORIZON BY HYDROMETER)[a]

Soil type	2-1 mm	1000-500 μ	500-250 μ	250-100 μ	100-50 μ	Total 200-50 μ	Total (silt) 50-2 μ	Total (clay) <2.0 μ
Anclote loamy fine sand	0.1	2.7	22.4	57.4	2.4	85.0	11.6	3.4
Apopka sand	0.2	4.0	38.3	49.7	3.1	95.3	3.0	1.7
Arredondo sand	0.5	8.1	40.7	38.8	5.1	93.2	4.4	2.4
Astatula fine sand	--	2.4	10.4	69.3	15.0	97.0	2.5	0.5
Basinger fine sand	0.3	6.2	27.6	54.5	3.5	92.1	6.7	1.2
Candler sand	--	2.9	45.0	46.0	2.0	95.9	2.7	1.4
Cocoa sand	0.5	13.1	32.8	44.6	2.8	93.8	3.2	3.0
Eau Gallie fine sand	--	2.3	24.5	61.8	3.6	92.2	6.0	1.8
Felda sand	--	4.3	43.9	45.7	3.1	97.0	2.1	0.9
Lake Sand	2.4	16.5	44.1	28.5	2.7	94.2	3.5	2.3
Margate fine sand	0.1	6.6	35.3	53.4	1.6	97.0	1.5	1.5
Myakka fine sand	0.1	3.2	27.3	64.2	1.7	96.5	2.3	1.2
Oldsmar sand	--	4.0	44.8	40.7	6.7	96.2	2.6	1.2
Ona fine sand	--	1.0	13.8	53.2	23.2	91.2	6.3	2.5
St. Lucie fine sand	--	1.6	21.4	72.7	1.2	96.9	2.6	0.5
Unnamed fine sand	0.1	0.3	1.2	67.1	19.7	88.4	8.9	2.7

[a]Calhoun et al., 1974.

agricultural worker exposure to particulate matter could be at least 10 times greater in California compared to Florida.

These data justify the following conclusions: (1) sample integrity through manual leaf handling and high air flow pesticide stripping remain questions with the vacuum technique for pesticides other than parathion. Consequently, air flow stripping must be assessed for individual pesticides, (2) both the Gunther et al. dislodgeable technique and vacuum technique are biased toward estimates of airborne exposure of agricultural workers due to the transfer mechanics of soil particulates from leaf surface to worker, (3) the two techniques are highly correlated for both residue and particulate data trends, and (4) the residue obtained with the dislodgeable technique appears to be more concentrated on a "per particulate" basis.

The primary difference between the vacuum and dislodgeable residue techniques was the amount of pesticide recovered from the leaf surface. This difference reflects the stringency of the method used to recover the surface pesticide residue. The Gunther et al. dislodgeable residue technique is consequently more representative of the total potential leaf surface residue hazard to agricultural workers and should remain the residue technique to use for worker safety reentry data. However, actual exposure needs to be correlated to the potential as determined by this dislodgeable method, in order to truly assess residue hazard during reentry.

SMALL PLOT EXPERIMENT

Weather varied appreciably comparing the two experiments. Cumulative average temperature (°C) after 29 days was 581.26 (exp. 1) and 840.4 (exp. 2). Cumulative relative humidity (hr over 90%) was 336.5 (exp. 1) and 472.5 (exp. 2). Cumulative solar incidence (gm cal cm^{-2} min^{-1}) was twice as great in experiment 1 (23,251.9) compared to experiment 2 (10,518.9). There was no rainfall in experiment 1 and 12.71 cumulative inches during experiment 2. Cumulative leaf wetness (hr) was 206.68 (exp. 1) and 371.81 (exp. 2).

In previous studies, leaf, fruit, and soil surfaces residue disappearance was correlated with cumulative weather variables (Nigg et al. 1977, 1978, 1979). In this series of experiments, however, time alone was so similar to a weather model in explaining residue variation that a time base was used for these data. Figure 6 illustrates the difficulty. Time correlates extremely well with each of the cumulative weather variables and weather variables correlate with one another. It is impossible in this situation to determine the relative importance of any individual weather variable to pesticide disappearance in a given experiment.

There were no differences in the rate of disappearance of any individual residue from fruit and leaf surfaces. These data have been combined in Figs. 7 through 10. Individual residue determinations are in Tables 16 and 17. Pesticide disappearance has been represented as first-order (Gunther and Blinn, 1955), first-order-weather (Nigg et al., 1977, 1978, 1979) and diffusion kinetics (Stamper et al., 1979). The diffusion ln-ln representation of the data (Stamper et al., 1979) was the best statistically and all of the R^2 values of 0.768 to 0.999 are significant at the 0.01 level. The figures

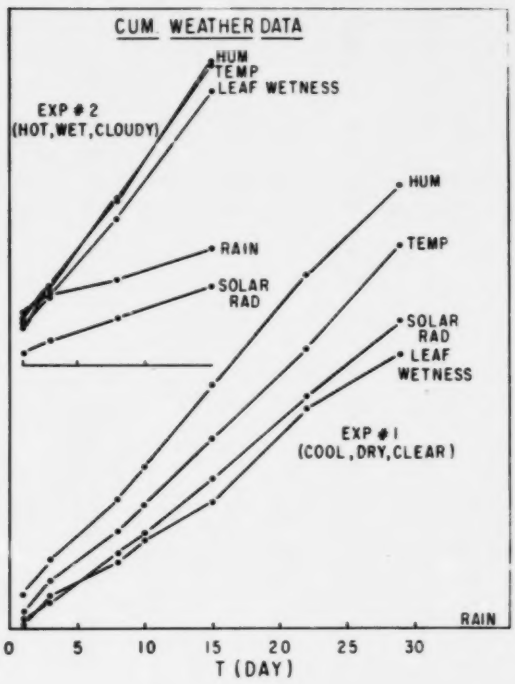

Figure 6. Cumulative weather variables vs. time in days. Cumulative average temperature (°C), cumulative relative humidity (hr over 90%); Cumulative solar incidence (gm cal cm^{-2} min^{-1}), cumulative leaf wetness (hr); cumulative rainfall (inches). There are no actual units on the y-axis for comparative purposes.

(7-10) indicate a moderate weather effect, i.e., larger slopes (faster disappearance) in experiment 2 under hot, wet, cloudy conditions. Based on differences in these slopes, oxydemetonmethyl shows the greatest weather effect, malathion is intermediate and dioxathion and dialifor show a much smaller, but similar effect of weather on their disappearance.

The slope of this disappearance should theoretically be 1.5 (Stamper et al., 1979). Malathion slopes were very close to this value (1.571, 1.027, Fig. 7), similar to results obtained for ethion, and parathion in previous experiments (Stamper et al., 1979). Oxydemetonmethyl had a slope of 1.328 in experiment 2, but only 0.355 in experiment 1; dialifor and dioxathion were very similar with slopes of about 0.35 to 0.60. Disappearance rates of individual materials were in the order malathion >> oxydemetonmethyl > dialifor $\geq$ dioxathion.

TABLE 16. SMALL PLOT EXPERIMENT 1--PESTICIDE RESIDUES (MAR. 14-APRIL11, 1978)

		Day 1	Day 3	Day 8
Leaves $\mu g/cm^2$	Delnav	.3 ± .03[a]	.2 ± .01	.2 ± .02
	Malathion/ M'oxon	.5 ± .2/.004 ± .0007	.1 ± .03/.002 ± .0005	.08 ± .03/.004 ± .0005
	MSR	.2 ± .02	.3 ± .1	.15 ± .1
	Torak	.6 ± .08	.5 ± .07	.3 ± .03
Fruit $\mu g/cm^2$	Delnav	.6 ± .1	.4 ± .09	.4 ± .08
	Malathion/ M'oxon	.4 ± .1/.01 ± .01	.2 ± .03/.005 ± .001	.1 ± .05/.006 ± .005
	MSR	.5 ± .03	.5 ± .08	.4 ± .07
	Torak	1.1 ± .5	1.1 ± .1	.5 ± .08
Soil vacuum (middle) ppm	Delnav	1.4 ± .7	.5 ± .4	.2 ± .08
	Malathion/ M'oxon	1.8 ± 1.8/.1 ± .1	.6 ± .7/.06 ± .08	.4 ± .2/.09 ± .01
	MSR	4.5 ± 2.3	.1 ± .2	.05 ± .04
	Torak	4.1 ± 1.6	3.2 ± 2.2	1.3 ± 1.2
Soil vacuum (dripline) ppm	Delnav	23.8 ± 13.4	27.4 ± 11.5	2.6 ± 2.1
	Malathion/ M'oxon	14.7 ± 7.9/.6 ± .3	10.2 ± 7.1/.2 ± .2	3.2 ± 2.4/.5 ± .3
	MSR	63.1 ± 23.8	1.6 ± 1.1	.7 ± .3
	Torak	21.5 ± 10.7	35.0 ± 15.0	4.7 ± 6.4

[a]Results expressed as mean ± S.D. (four replications). CONTINUED

TABLE 16. (CONTINUED)

		Day 10	Day 15	Day 22
Leaves $\mu g/cm^2$	Delnav	.1 ± .05	.1 ± .01	.1 ± .03
	Malathion/ M'oxon	.03 ± .01/.002 ± .001	.02 ± .01/.003 ± .001	.01 ± .04/.002 ± .002
	MSR	.1 ± .04	.1 ± .02	.06 ± .02
	Torak	.2 ± .02	.2 ± .03	.2 ± .04
Fruit $\mu g/cm^2$	Delnav	.3 ± .03	.3 ± .03	.2 ± .05
	Malathion/ M'oxon	.09 ± .05/.007 ± .002	.04 ± .008/.005 ± .001	.03 ± .02/.003 ± .004
	MSR	.3 ± .03	.4 ± .009	.3 ± .06
	Torak	.4 ± .1	.4 ± .09	.2 ± .06
Soil vacuum (middle) ppm	Delnav	.02 ± .02	.1 ± .03	.05 ± .02
	Malathion/ M'oxon	.1 ± .07/.02 ± .03	.08 ± .05/.02 ± .02	.1 ± .1/ND
	MSR	.7 ± .3	0	0
	Torak	1.3 ± 1.4	.8 ± .6	.3 ± .2
Soil vacuum (dripline) ppm	Delnav	6.5 ± 4.4	2.3 ± 1.8	.7 ± .1
	Malathion/ M'oxon	7.7 ± 3.9/2.2 ± 1.1	1.0 ± .5/.2 ± .3	4.1 ± 6.1/1.3 ± 2.2
	MSR	4.3 ± 7.0	.5 ± .3	4.7 ± 5.8
	Torak	27.0 ± 13.8	20.4 ± 11.4	13.0 ± 10.3

(CONTINUED)

TABLE 16. (CONTINUED)

		Day 29
Leaves $\mu g/cm^2$	Delnav	0.5 ± .02
	Malathion/ M'oxon	.01 ± .005/.001 ± .001
	MSR	.03 ± .03
	Torak	.2 ± .04
Fruit $\mu g/cm^2$	Delnav	.2 ± .03
	Malathion/ M'oxon	.02 ± .006/.002 ± .001
	MSR	.4 ± .1
	Torak	.3 ± .2
Soil vacuum (middle) ppm	Delnav	.06 ± .02
	Malathion/ M'oxon	.06 ± .04/ND
	MSR	0
	Torak	.2 ± .1
Soil vacuum (dripline) ppm	Delnav	.5 ± .5
	Malathion/ M'oxon	.9 ± 1.5/.7 ± 1.3
	MSR	1.2 ± 1.2
	Torak	7.0 ± 2.5

TABLE 17. SMALL PLOT EXPERIMENT 2--PESTICIDE RESIDUES (JULY 11-26, 1978)

		Day 1	Oxon	Day 3	Oxon
Leaves ($\mu g/cm^2$)	Delnav	.04 ± .02[a]		.04 ± .01	
	Malathion	.006 ± .003	ND	.004 ± .001	ND
	Metasystox-R (sulfone)	.003 ± .002		.001 ± .0004	
	Torak	.1 ± .02		.07 ± .02	
Fruit ($\mu g/cm^2$)	Delnav	.06 ± .03		.03 ± .01	
	Malathion	.006 ± .002	ND	.001 ± .0004	ND
	Metasystox-R (sulfone)	.005 ± .002		.0008 ± .0003	
	Torak	.2 ± .05		.1 ± .02	
Soil Vacuum middle (ppm)	Delnav	.1 ± .02		.07 ± .06	
	Malathion	.01 ± .02	ND	ND	ND
	Metasystox-R (sulfone)	ND		ND	
	Torak	.3 ± .05		.07 ± .02	
Soil Vacuum dripline (ppm)	Delnav	1.2 ± .2		.9 ± .1	
	Malathion	.4 ± .07	ND	ND	ND
	Metasystox-R (sulfone)	ND		ND	
	Torak	8.2 + 2.9		6.1 + 2.0	

[a]Results expressed as mean ± S.D. (four replications).

(CONTINUED)

TABLE 17. (CONTINUED)

		Day 8	Oxon	Day 15	Oxon
Leaves ($\mu g/cm^2$)	Delnav	.02 ± .006		.01 ± .001	
	Malathion	.0005 ± .001	ND	--	
	Metasystox-R (sulfone)	.0003 ± .0002		.0006 ± .0002	
	Torak	.04 ± .01		.02 ± .005	
Fruit ($\mu g/cm^2$)	Delnav	.03 ± .01		.01 ± .0005	
	Malathion	.0001 ± .0002	ND	--	
	Metasystox-R (sulfone)	.0002 ± .0002		.0006 ± .0008	
	Torak	.1 ± .02		.03 ± .02	
Soil Vacuum middle (ppm)	Delnav	.02 ± .005		.4 ± .07	
	Malathion	ND	ND	--	--
	Metasystox-R (sulfone)	ND		ND	
	Torak	.09 ± .04		.1 ± .09	
Soil Vacuum dripline (ppm)	Delnav	.8 ± .2		1.1 ± .4	
	Malathion	ND	ND	--	--
	Metasystox-R (sulfone)	ND		ND	
	Torak	4.8 ± 2.7		8.4 ± 2.1	

[a]Results expressed as mean ± S.D. (four replications).

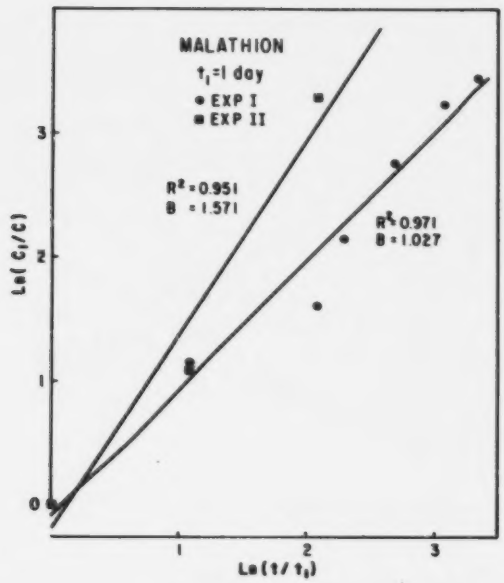

Figure 7. Ln-ln plot of combined malathion fruit and leaf surface residues. Initial concentration (day 1) of malathion fruit: 0.4 $\pm$ 1 µg/cm^2 experiment 1, leaves 0.5 $\pm$ 0.12 µg/cm^2 experiment 1; fruit 0.0006 $\pm$ 0.002 µg/cm^2 experiment 2, malathion leaves 0.006 $\pm$ 0.003 µg/cm^2 experiment 2.

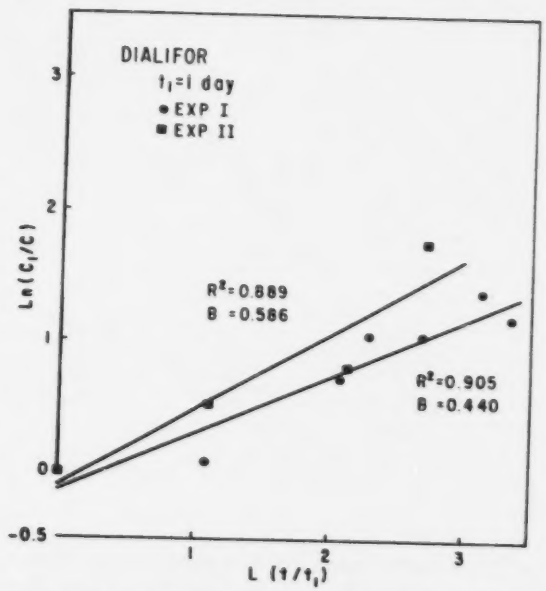

Figure 8. Ln-ln plot of combined dialifor fruit and leaf surface residues. Initial concentration (day 1) of dialifor fruit 1.1 $\pm$ 0.5 µg/cm^2 experiment 1, leaves 0.6 $\pm$ 0.08 experiment 1; fruit 0.2 $\pm$ 0.05 µg/cm^2 experiment 2, leaves 0.1 $\pm$ 0.02 µg/cm^2 experiment 2.

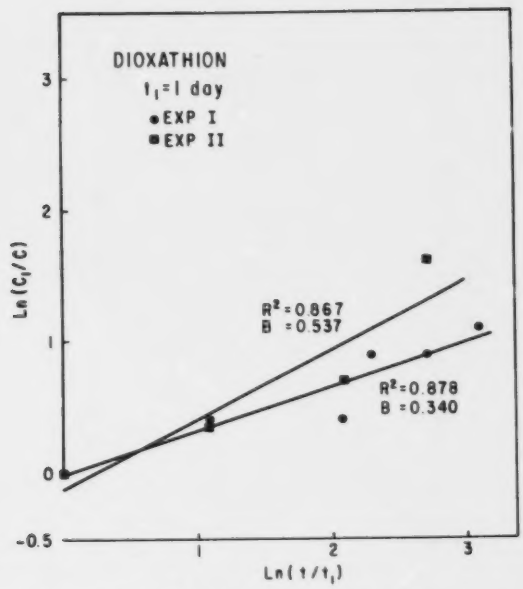

Figure 9. Ln-ln plot of combined dioxathion fruit and leaf surface residues. Initial concentration (day 1) of dioxathion fruit 0.6 ± 0.1 µg/cm^2 experiment 1, leaves 0.3 ± 0.003 µg/cm^2 experiment 1; fruit 0.06 to 0.03 µg/cm^2 experiment 2, leaves 0.01 ± 0.02 experiment 2.

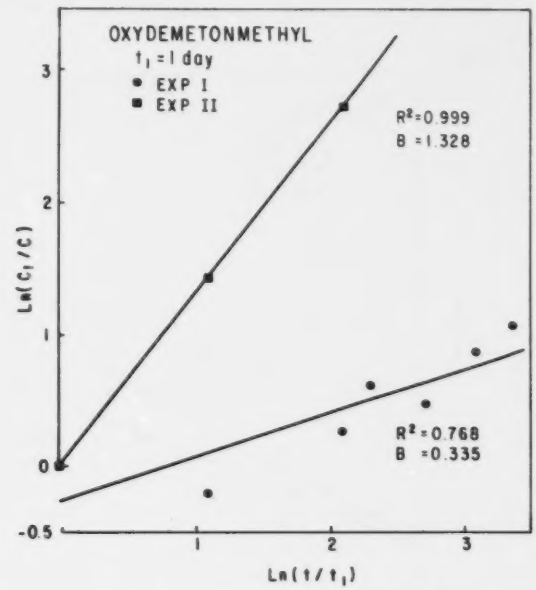

Figure 10. Ln-ln plot of combined oxydemetonmethyl fruit and leaf surface residues. Initial concentration (day 1) of oxydemetonmethyl fruit 0.5 ± 0.03 µg/cm^2 experiment 1, leaves 0.2 ± 0.02 µg/cm^2 experiment 1; fruit 0.005 ± 0.002 µg/cm^2 experiment 2; leaves 0.003 ± 0.002 µg/cm^2 experiment 2.

Figure 11 presents the malaoxon data for leaf and fruit surfaces in experiment 1 (dry, cool, clear conditions). Actual residue values are noted by each point. The line is the percent malaoxon residue (malaoxon/malathion x 100). The actual quantity of malaoxon was surprisingly constant over the course of this experiment. In previous experiments an initial rise of oxon metabolite of parathion, carbophenothion and ethion was evident (Nigg et al., 1977, 1978, 1979) followed by a decrease. Since the parent compound, malathion, exhibited a steady disappearance, the percentage of malaoxon increased (Fig. 11). A small production of malaoxon during the extraction process might account for these data, but no malaoxon was detected in malathion-fortified fruit and leaf washes thus eliminating this possibility. No malaoxon was detected during experiment 2 (wet, hot, cloudy conditions). This is similar to results of previous experiments (Nigg et al., 1977, 1978, 1979) and supports the supposition that hydrolysis is central to disappearance of the oxon metabolites of the organophosphates (Gunther et al., 1977, Spencer et al. 1975).

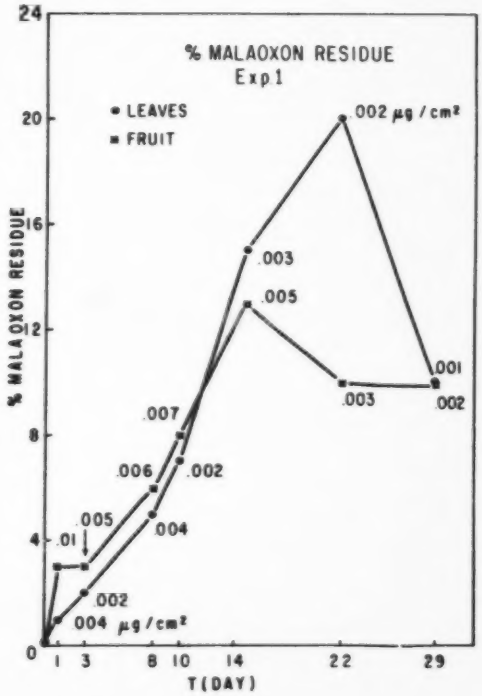

Figure 11. % malaoxon residue. (Malaoxon/malathion x 100). Actual values are next to each point in $\mu g/cm^2$.

Fruit and leaf surface organophosphate residue data are so similar that only one type of sample need be taken for worker reentry residue data. Leaf samples are much more convenient to process and extract compared to fruit (Gunther et al., 1977, Iwata et al., 1977) and the variation for both types of sample is essentially the same (Table 18). We suggest that fruit samples be eliminated as a requirement for worker reentry data for the registration of organophosphate pesticides.

The physical and chemical characteristics of individual pesticides coupled with the effects of environmental conditions on these characteristics determine disappearance rate. Theory suggests that the individual diffusion coefficient or vapor pressure may be the most important physical chemical characteristics in residue disappearance (Stamper et al., 1979) and environmental effects on these chemical characteristics warrant investigation.

TABLE 18. SMALL PLOT FRUIT AND LEAF SURFACE RESIDUES COEFFICIENT OF VAIRATION

Experiment 1	Day 1	Day 3	Day 8	Day 10	Day 15	Day 22	Day 29	Avg.
Dioxathion								
Leaves	10	5	10	50	10	30	40	22
Fruit	17	23	20	10	10	25	15	17
Malathion								
Leaves	40	30	38	33	50	400	50	91
Fruit	25	15	50	56	20	67	30	38
Oxydemetonmethyl								
Leaves	10	33	67	25	20	33	100	41
Fruit	6	16	18	10	2	20	25	14
Dialifor								
Leaves	13	14	10	10	15	20	20	15
Fruit	45	9	16	25	23	30	67	31
Experiment 2								
Dioxathion								
Leaves	50	25	30		10			29
Fruit	33	33	33		5			26
Malathion								
Leaves	50	25	200		--			92
Fruit	33	25	200		--			86
Oxydemetonmethyl								
Leaves	67	40	67		33			52
Fruit	40	38	100		133			78
Dialifor								
Leaves	20	29	25		25			25
Fruit	25	20	20		67			33
						Leaf Avg.		46
						Fruit Avg.		40

TABLE 19. CONVERSION OF PESTICIDE APPLICATION RATES FROM ENGLISH TO METRIC SYSTEM

(A) English	(B) Metric	To convert from English to metric, multiply column A by
Pounds	Kilograms	0.454
Gallons	Liters	3.79
Acre	Hectare	0.405
Pounds/acre	Kg/ha	1.12

REFERENCES

Adams, J. D., Y. Iwata, and F. A. Gunther. 1976. The effect of dust derived from several soil types on the dissipation of parathion and paraoxon dislodgable residues on citrus foliage. Bull Environ Contam. Toxicol. 15:547-554.

Blinn, R. C., G. E. Carman, W. H. Ewart, and F. A. Gunther. 1959. Residual behavior of various insecticides on and in lemons and oranges. J. Econ. Entomol. 52:42-44.

Calhoun, F. G., V. W. Carlisle, R. E. Caldwell, L. W. Zelazuy, L. C. Hammond, and H. L. Breland. 1974. Characterization data for selected Florida soils. Univ. Fla., IFAS, USDA Soil Conserv. Service. 293 pp.

Gunther, F. A., J. H. Barkley, and W. E. Westlake. 1974. Worker environment research II. Sampling and processing techniques for determining dislodgable pesticide residues on leaf surfaces. Bull. Environ. Contam. Toxicol. 12:641-644.

Gunther, F. A., Y. Iwata , G. E. Carman, and C. A. Smith. 1977. The citrus reentry problem: Research on its causes and effects, and approaches to its minimization. Residue Rev. 67:1-139.

Gunther, F. A., W. E. Westlake, J. H. Barkley, W. Winterlin, and L. Langbehn. 1973. Establishing dislodgable pesticide residues on leaf surfaces. Bull. Environ. Contam. Toxicol. 9:243.

Guthrie, F. E., J. J. Domanski, A. R. Main, D. G. Sanders, and R. R. Monroe. 1974. Use of mice for initial approximation of reentry intervals into pesticide-treated fields. Arch.Environ. Contam. Toxicol. 2:233-242.

Iwata, Y., M. E. Dusch, W. E. Westlake, and F. A. Gunther. 1975. Behavior or five organophosphate pesticides in dust derived from several soil types. Bull. Environ. Contam. Toxicol. 14:49-56.

Iwata, Y., J. B. Knaak, R. C. Spear, and R. B. Foster. 1977. Worker reentry into pesticide-treated crops. I. Procedure for the determination of dislodgable pesticide residues on foliage. Bull Environ. Contam. Toxicol. 18:649-655.

Iwata, Y., W. E. Westlake, and F. A. Gunther. 1973. Persistence of parathion in six California soils under laboratory conditions. Arch. Environ. Contam. Toxicol. 1:84-96.

Leffingwell, J. T., R. C. Spear, and D. Jenkins. 1975. The persistence of ethion and zolone residues on grape foliage in the central valley of California. Arch. Environ. Contam. Toxicol. 3:40-54.

Liu, B. Y. H., and K. W. Lee. 1976. Efficiency of membrane and nuclepore filters for submicrometer aerosols. Environ. Sci. Technol. 10:345-350.

Megaw, W. J., and R. D. Wiffen. 1963. The efficiency of membrane filters. Int. J. Air Wat. Poll. 7:501-509.

Miles, J. W., L. E. Fetzer, and G. W. Pearce. 1970. Collection and determination of trace quantities of pesticides in air. Environ. Sci. Technol. 4:420-425.

Morrison, D. F. 1967. Multivariate Statistical Methods. p. 104. McGraw-Hill, NY. 338 pp.

Natusch, D. F. S., and J. R. Wallace. 1974. Urban aerosol toxicity: The influence of particle size. Science 186:695-699.

Nigg, H. N., J. C. Allen, R. F. Brooks, G. J. Edwards, N. P. Thompson, R. W. King, and A. H. Blagg. 1977a. Dislodgeable residues of ethion in Florida citrus and relationships to weather variables. Arch. Environ. Contam. Toxicol. 6:257-267.

Nigg, H. N., J. C. Allen, and R. F. Brooks. 1977b. Weather and pesticide residues. Proc. Int. Soc. Citriculture 2:437-441.

Nigg, H. N., J. C. Allen, R. W. King, N. P. Thompson, G. J. Edwards, and R. F. Brooks. 1978. Dislodgeable residues of parathion and carbophenothion in Florida citrus: A weather model. Bull Environ. Contam. Toxicol. 19:578-588.

Nigg, H. N., J. C. Allen, and R. W. King. 1979. Behavior of parathion residues in the Florida'Valencia' orange agroecosystem. J. Agric. Food Chem. 27:578-582.

Patterson, E. M., and D. A. Gillette. 1977a. Measurements of visibility vs. mass-concentration for airborne soil particles. Atmospheric Environ. 11:193-196.

Patterson, E. M., and D. A. Gillette. 1977b. Commonalities in measured size distributions for aerosols having a soil-derived component. J. Geophys. Res. 82:2074-2082.

Patterson, E. M., D. A. Gillette, and G. W. Grams. 1976. The relation between visibility and the size-number distribution of airborne soil particles. J. Appl. Meteorol. 15:470-478.

Popendorf, W. J., and J. T. Leffingwell. 1978. Natural variations in the decay and oxidation of parathion foliar residues. J. Agric. Food.

Chem. 26:437-441.

Popendorf, W. J., and R. C. Spear. 1974. Preliminary survey of factors affecting the exposure of harvesters to pesticide residues. Amer. Ind. Hyg. Assoc. J. 35:374-380.

Popendorf, W. J., R. C. Spear, and S. Selvin. 1975. Collecting foliar pesticide residues related to potential airborne exposure of workers. J. Agric. Food Chem. 9:583-585.

Schultze, R. E. 1976. A physically based method of estimating solar radiation from suncards. Agric. Meteorol. 16:85-101.

Serat, W. F. 1973. Calculation of a safe reentry time into an orchard treated with a pesticide chemical which produces a measureable physiological response. Arch. Environ. Contam. Toxicol. 1:170-181.

Serat, W. F., and J. B. Bailey. 1974. Estimating the relative toxicologic potential of each pesticide in a mixture of residues on foliage. Bull. Environ. Contam. Toxicol. 12:682-686.

Serat, W. F. 1978. Estimating a worker entry interval for the carbamate pesticide furadan 4E insecticide. Arch. Environ. Contam. Toxicol. 7:1-11.

Serat, W. F., D. C. Mengle, H. P. Anderson, E. Kahn, and J. B. Bailey. 1975. On the estimation of worker entry intervals into pesticide treated fields with and without the exposure of human subjects. Bull. Environ. Contam. Toxicol. 13:506-512.

Sherma, J., and T. M. Shafik. 1975. A multiclass, multiresidue analytical method for determining pesticide residues in air. Arch. Environ. Contam. Toxicol. 3:55-71.

Spear, R. C. 1978. Organophosphate residue poisoning among agricultural fieldworkers in the Western United States: Towards a strategy for a long-term solution. Center for Resource and Environmental Studies Report AS/R18, Australia National Univ. 35 pp.

Spear, R. C., Y. S. Lee, J. T. Leffingwell, and D. Jenkins. 1978. Conversion of parathion to paraoxon in foliar residues: Effects of dust level and ozone concentration. J. Agric. Food Chem. 26:434-436.

Spear, R. C., W. J. Popendorf, J. T. Leffingwell, and D. Jenkins. 1975. Parathion residues on citrus foliage. Decay and composition as related to worker hazard. J. Agric. Food Chem. 23:808-810.

Spear, R. C., W. J. Popendorf, J. T. Leffingwell, T. H. Milby, J. E. Davies, and W. F. Spencer. 1977. Fieldworkers response to weathered residues of parathion. J. Occ. Med. 19:406-410.

Spencer, W. F., M. M. Cliath, K. R. Davis, R. C. Spear, and W. J. Popendorf. 1975. Persistence of parathion and its oxidation to paraoxon on the soil surface as related to worker reentry into treated crops. Bull. Environ. Contam. Toxicol. 14:265-272.

Spencer, W. F., Y. Iwata, W. W. Kilgore, and J. B. Knaak. 1977. Worker reentry into pesticide-treated crops. II. Procedure for the determination of pesticide residues on the soil surface. Bull. Environ. Contam. Toxicol. 18:656-662.

Stamper, J. H., H. N. Nigg, and J. C. Allen. 1979. Organophosphate insecticide disappearance from leaf surfaces: An alternative to first-order kinetics. Environ. Sci. Technol. 13:1402-1405.

Thornton, J. S., T. J. Olsen, and K. Wagner. 1977. Determination of residues of metasystox-R and metabolite in plant and animal tissues and soil. J. Agric. Food Chem. 25:573-576.

Turrell, F. M. 1961. Growth of the photosynthetic area of citrus. Bot. Gaz. 122:284-298.

Van Dyk, L. P., and K. Visweswariah. 1975. Pesticides in air: Sampling methods. Residue Rev. 55:91-134.

Westlake, W. E., F. A. Gunther, and G. E. Carman. 1973. Worker environment research: dioxathion (Delnav^{R}) residues on and in orange fruits and leaves, in dislodgable particulate matter, and in the soil beneath sprayed trees. Arch. Environ. Contam. Toxicol. 1:60-83.

Wolfe, H. R., J. F. Armstrong, D. C. Staiff, S. W. Comer, and W. F. Durham. 1975. Exposure of apple thinners to parathion residues. Arch. Environ. Contam. Toxicol. 3:257-267.

BIBLIOGRAPHY

Nigg, H. N., N. P. Thompson, J. C. Allen, and R. F. Brooks. 1977. Worker reentry and residues of ethion, parathion, and carbophenothion (Trithion) on Florida citrus. Proc. Fla. State Hort. Soc. 90:19-21.

Nigg, Herbert N., and Jon C. Allen. 1979. A comparison of time and time-weather models for predicting parathion disappearance under California conditions. Environ. Sci. Technol. 13:231-233.

Nigg, Herbert N. 1979. Comparison of pesticide and particulate recoveries with the vacuum and dislodgeable surface pesticide residue techniques. Arch. Environ. Contam. Toxicol. 8:369-381.

Nigg, H. N. James A. Reinert, and G. E. Fitzpatrick. 1979. Weather-dependent residue behavior of malathion in Florida citrus varieties. Bull. Environ. Contam. Toxicol. 21:697-702.

Nigg, H. N., and J. H. Stamper. 1980. Comparative disappearance of dioxathion, malathion, oxydemetonmethyl and dialifor from Florida citrus leaf and fruit surfaces. J. Econ. Entomol. (Submitted).